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The fate of phosphorus and molybdenum after biosolids, swine manure and triple superphosphate were applied to a soil

Jorge David Hernandez
Iowa State University

The fate of phosphorus and molybdenum after biosolids, swine manure and triple superphosphate were applied to a soil

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Jorge David Hernandez

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Program of Study Committee:
Randy Killorn, Major Professor
Dale Farnham
Ricardo Salvador
Lee Burras
Michael Thompson

Iowa State University

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Graduate College
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Jorge David Hernandez

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Major Professor

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For the Major Program

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CHAPTER 1. GENERAL INTRODUCTION

DISSERTATION ORGANIZATION

This dissertation is organized into five chapters. The first chapter is the general introduction to the dissertation. Chapters 2 through 4 are manuscripts that will be submitted to the Journal of Environmental Quality for publication. Each individual manuscript has an abstract, introduction, materials and methods, results and discussion, summary and conclusions. The last chapter is the general conclusion.

CHAPTER 1. GENERAL INTRODUCTION

The use of biosolids (BS) and manure as sources of nutrients for crop production is a practice that is currently in use, more as a way of disposing of waste than for its efficient utilization. The use of BS and manure as a source of nutrients is of great importance in areas where sustainable agriculture is a practice of interest. Biosolids and swine manure (SM) have been used as sources of nitrogen (N) and phosphorus (P) for years. However, the proportions and amounts that can be used by crops and their consequences in the soil-crop system remain unclear (Frossard et al., 1996).

An increase of soil P above concentrations required for crop production is a concern. High P concentrations in the soil might produce an imbalance in the soil chemical equilibrium and may enhance Mo mobility (Xie and McKenzey, 1991). These two elements, P and Mo, pose an environmental risk when present in large amounts in ecosystems. Molybdenum, when present in relatively large quantities,

may induce toxicity in the biological chain. Molybdate is present in BS and SM but not in high concentrations. However, due to the large amounts of BS and SM applied to fields, its absolute amounts applied can be high.

Phillips and Grant (1994) showed that use of BS in crop production has a minimal effect on agricultural ecosystems when they are applied at appropriate rates. Similarly, Summers et al. (1979) conducted a study evaluating the potential of P leaching in soils in Pennsylvania and minimal P leaching was observed. However, other studies have shown that the continuous use of BS might produce a build up of heavy metals and P in soil profiles (Peterson et al., 1994; Sui et al., 1999).

An increase of P dissolved in the soil solution might increase the movement of P out of the sorption sites. Repeated manure application to soil has been shown to increase the potential for P leaching (Chang et al., 1991; James et al., 1996). Sui and Thompson (2000), in a lab study showed that the application of BS to soils increased the P concentration in solution, decreasing the ability of the soil to sorb P. Phosphorus and Mo are present in the soil primarily in anionic forms phosphate (HPO_4^{2-} and $H_2PO_4^-$) and molybdate (MoO_4^{2-}) and they have differences in the affinity for sorption sites. Both single sorbate and multisorbate systems studies indicated phosphate is preferred over molybdate on oxide sorption sites (Ryden, et al., 1987). Consequently plant Mo uptake is enhanced by the presence of soluble P (Xie and MacKenzey, 1991).

Numerous factors contribute to Mo and P availability in soil systems and crop uptake. Phosphorus and Mo are affected by soil pH, organic matter in the soil, interaction with other nutrients, and plant species (Gupta, 1997). Lab studies have shown that P tends to compete with Mo for surface sorption sites in the soil (Xie and Mackenzie, 1991). Other studies suggest that the P/Mo relationship might change depending on the soil type and soil pH under consideration (Karimian and Cox, 1978; Balistrieri and Chao, 1990; Bibak and Borgaard, 1994).

Most researchers have reported that Mo has a low mobility due to its low concentration in soils. However, plant availability of soil Mo increases at pH higher than 6.0 in high-P-test soils with high organic matter content (Jones et al., 1990). The literature does not report much information about the possible effects of soil P build up on Mo sorption onto the soil. A release of Mo from the soil sorption sites into the soil solution might increase plant availability. Even though an excess of Mo does not seem to cause toxicity in crops in field conditions (Gupta and Lipsett, 1981), increases of Mo crop uptake might result in a serious risk for livestock production. An excess of Mo in livestock diet may produce a disorder called molybdenosis.

Molybdenosis is a malady that may affect livestock and particularly cattle are highly sensitive to this abnormality. It is characterized by the presence of high amounts of Mo and sulfur combined with low concentration of copper in animal feed. This condition enhances a copper deficiency. Increasing Mo plant availability to soybean and corn might increase this risk and eventually make such crops unsuitable for animal consumption (Gupta and Lipsett, 1981; Neuman et al., 1987).

Little in the literature addresses the effect of the application of triple super phosphate (TSP), SM, and BS to high P soils, on Mo availability and plant uptake. Very little has been done to study the effect of BS and SM application on the availability of Mo in the soil-water-plant system. Therefore, the effect of increasing soluble P on Mo availability in high STP soils deserves further investigation.

The objective of this study is to determine the effect of the application of BS, SM, and TSP to high soil test phosphorus (STP) soils on P mobility and its effect on soybean and corn plant Mo accumulation.

CHAPTER 2.THE FATE OF PHOSPHORUS AND MOLYBDENUM AFTER BIOSOLIDS, SWINE MANURE AND TRIPLE SUPERPHOSPHATE WERE SOIL APPLIED: AN INCUBATION STUDY

A paper prepared for submission to the Journal of Environmental Quality

J. D. Hernandez*, R. Killorn **

Abstract

The effect of applying phosphorus (P) on high P test soils (STP) is a concern due to possible changes in water, soil, and crop quality. Increasing P in the soil may change relationships with other nutrients such as molybdenum (Mo). The purpose of this study was to determine the effects of the application of triple superphosphate (TSP), swine manure (SM), and biosolids (BS) on soil P forms and extractable Mo. An incubation study was conducted in a chamber with controlled temperature and light. The treatments consisted of mixing 10 g of soil from 4 different depths with TSP, SM, and BS at a low and a high rate. A sequential fractionation for inorganic and organic P forms was performed. Soil extractable Mo was determined as well. There were differences in extractable Mo after treatments were applied, and the BS application always produced the highest values. Soil P was higher in the BS treatment than in the SM and TSP treatments in all P fractions. Increasing P rate increased soil extractable P and Mo in soils. Extractable Mo within the treatments was not affected by soil properties with soil depth. The application of BS, SM, and TSP to high STP soil resulted in differences in extractable P fractions in the soil. The proportion of soil P fractions were: NaOH-Po > HCl-P > $NaHCO_3$-Pi > H_2SO_4-P.

* Hernandez, J. D. Research Assistant. Dept. Agronomy, Iowa State University, Ames IA 50010
** Killorn, R. Professor. Dept. Agronomy, Iowa State University, Ames IA, 50010

The $NaHCO_3$-Pi, NaOH-Pi and HCl-P fractions increased in BS treatments more than in other treatments. This suggests that BS have the potential to increase other P fractions due to the addition of Al and Fe associated with P sorption sites and an increase in labile P. Swine manure and BS increased the HCl-P, suggesting that they either enhanced Ca-P bonding or contained Ca-phosphate. Most soil P fractions were affected by the P source x rate interaction. This indicates that an increase of P rate affected P extraction differently, depending upon the source.

Introduction

The use of BS and SM as sources of nutrients for crop production is a practice that is currently in use, more as a way of disposing of waste than for its efficient utilization as source of nutrients. Repeated SM applications on soils might increase the movement of P out of sorption sites, due mainly to P saturation (Chang et al., 1991; James et al., 1996). Thus, soil under repeated manure and biosolids application has shown the potential for P leaching (Chang et al., 1991; James et al., 1996). Sui and Thompson (2000), in a laboratory investigation, found that the application of biosolids at high levels to soils increased the P concentration in solution and decreased the ability of the soil to sorb P. Studies have shown that the continuous use of BS might produce a build up of P in soil (Peterson et al., 1994; Sui et al., 1999 a,b). Adding P to soils already high in P may induce changes in the interaction of P with other nutrients, particularly Mo (Gupta, 1997).

Phosphorus and Mo are present in the soil primarily in anionic forms of phosphate (HPO_4^- and $H_2PO_4^{2-}$) and molybdate (MoO_4^{2-}) (Reisenauer et al., 1973; Gupta, 1997). Phosphate and molybdate have different affinities to soil sorption sites (Ryden et al., 1987). Lab studies have shown that P competes with Mo for surface sorption sites in the soil (Xie and Mackenzie, 1991; Xie et al., 1993).

Molybdenum has low mobility in soils due to its low concentration in soil solution. However, increases of soil P, organic matter (OM) content, and pH values greater than 6 cause Mo mobility to increase (Jones et al., 1990; Gupta, 1997). Past research has not considered the possible effects of a build up of soil P on Mo sorption. A release of Mo from the soil sorption sites into the soil solution might result in increased plant availability of Mo (Bibak and Borggaard, 1994; Gupta, 1997).

Molybdenum, when present in relatively large quantities, may induce toxicity in the biological food chain (Gupta, 1997). Even though an excess of Mo does not seem to cause toxicity in crops under field conditions (Gupta and Lipsett, 1981), increases of Mo in plants may pose a risk for livestock production due to the potential to induce molybdenosis (Gupta, 1997).

Molybdenosis is a disease that severely affects the digestive track of livestock, particularly cattle (Dick, 1956). It is caused by an imbalance in animal diets due to the presence of relatively high amounts of Mo combined with low concentrations of Cu, which induces a Cu deficiency (Scott, 1972). Increasing plant Mo uptake in soybean and corn might make such crops unsuitable for animal consumption due to the risk of inducing molybdenosis. Typical parameter for

inducing molybdenosis have indicated Mo concentration greater than 5 mg kg^{-1} and a Cu:Mo ratio greater than 4 in animal feed (Gupta and Lipsett, 1981).

Sequential P fractionation can be a useful tool for determining small changes occurring in short-term incubation studies (Hedley et al., 1982). Often soil P fractionation is carried out to characterize the effects of P sources and soil nature on the potential availability and mobility of P in soils (McCoy et al., 1986). Fractionation of soil P will allow us to identify the predominant forms of organic and inorganic P present after application of BS, SM, and TSP. The type of P source and interactions with the soil system may change the "typical" P fractionation distribution in soils.

The common P fractions are related to the most common pools in soils. These forms are: 1) The readily available or labile inorganic P (Pi) and organic P (Po) in soil solution and weakly held to surface sites. The 0.5 M sodium bicarbonate ($NaHCO_3$) at pH 8.3 extracting solution has been used previously, and it has shown a good correlation between plant uptake and soil P extracted (Bowman and Cole, 1978). 2) The moderately available soil P fraction is associated with Fe and Al oxides sorption sites and with the most stable organic fraction. The 0.1 M sodium hydroxide (NaOH) extracting solution has been used, with acceptable statistical correlation with this soil P fraction (Ryden et al., 1977; Mc Laughlin et al., 1977). 3) The moderately available soil P fraction is associated with Ca and Mg oxide-like sites and apatite minerals. The 1.0 M hydrochloric acid (HCl) solution is a common extracting solution for this fraction (Williams et al., 1971; Williams et al., 1980). 4) The residual P, which is considered as the recalcitrant or very slowly released P

fraction, and is associated with stable crystalline and amorphous minerals and organic bonded P (Hedley et al., 1982).

Changes in cultivation practices, fertilizer rate, and the P source produce changes in the inorganic and organic soil P fractions (Hedley et al., 1982). Continuous application of BS to soils has changed the previous soil P fractionation (Soon and Bates, 1982). This change has been attributed to the addition of Al and Fe to BS that are already high in these substances due to either the industrial process or as a residual from the waste.

The objective of this study was to determine the effect of the application of BS, SM, and TSP to high soil-test P soil on extractable P fractions and its effect on Mo and P.

Materials and Methods

Representative soil samples from a Webster soil (Fine-loamy, mixed, superactive, mesic Typic Endoaquolls) were collected. This is a soil widely associated with corn and soybean production in Iowa. Soil pH (Thomas, 1996), sodium bicarbonate-P (Olsen et al., 1954), total organic carbon [TOC] (dry combustion with a CHN Analyzer, LECO Corp.), and calcium carbonate ($CaCO_3$) content (Sherrod et al., 2002) were determined prior to starting the incubation study (Table 1).

Soil samples from four different depths (0-10, 10-20, 20-30, 30-40 cm) were collected and brought to the lab. The soil was air-dried, then passed through a 2 x 2 mm non-galvanized screen. The screened soils were carefully mixed with BS, SM, and TSP. The P content of BS was 1.2 g kg^{-1}, SM 0.8 g kg^{-1} and TSP 193 g kg^{-1}.

The Mo concentration of BS was 14 mg kg^{-1}, SM 0.8 mg kg^{-1} (Table 2), and TSP contained no detectable Mo.

The treatments consisted of 10-g soil from each depth mixed with all the sources at P rates equivalent to "low application" of 28 mg of P per Kg of soil and to "high application" of 112 mg of P per Kg of soil. Equivalent P rates in each source were calculated based on the total P content (Table 2). The mixed samples were transferred into plastic containers. The soil was poured from the container onto a piece of brown paper, each source was added slowly with a pipette and rolled in all directions until thoroughly mixed. Then the mixture was returned into containers and placed into incubators.

The mixture was watered to approximate field capacity, and left in a growth chamber under conditions of 16 hours of light and 23 ± 2 °C for 33 and 66 days. Soil moisture content was checked based upon weight, and water was added as needed. The P sources BS and SM were digested using concentrate nitric acid/hydrogen peroxide digestion in a microwave system. The extract was analyzed for total content of aluminum and iron, using an atomic absorption spectrophotometer. Total calcium was determined using the Sherrod et al. (2002) methodology.

Phosphorus fractionation was accomplished using the sequential method of Hedley et al. (1982). A 0.5-g sample of soil-mixture from each treatment was transferred to a 50-ml centrifuge tube, and the same soil sample sequentially extracted (Fig. 1). Every soil P fraction was extracted using specific extracting solutions. A shaking time of 16 hours at 180 strokes per minute was required to

extract each fraction. All suspensions were centrifuged at 4200 x g for 10 minutes, and the supernatant filtered using analytical grade paper (Whatman no. 42).

The first extractant was 0.5 M sodium bicarbonate ($NaHCO_3$) adjusted to a pH of 8.2 (Bowman and Cole, 1978). At the end of the extraction time, 10 ml of the supernatant was analyzed for $NaHCO_3$ inorganic P ($NaHCO_3$)-Pi and 10 ml transferred into a volumetric flask and analyzed for total phosphorous. Total P analysis was performed using an oxidation and acid total digestion with concentrated sulfuric acid (H_2SO_4) and 50% hydrogen peroxide (H_2O_2) (Hach, 1988). The difference between total P and $NaHCO_3$-Pi is considered to be the organic P ($NaHCO_3$-Po) (Fig. 1).

The next sequential extraction of the original sample was with 0.1 M sodium hydroxide (NaOH) (Ryden et al., 1977; McLaughlin et al., 1977). A 10 ml subsample of the supernatant was analyzed for NaOH inorganic P (NaOH-Pi). Another 10-ml was transferred into a flask and acid/base total digestion was performed to obtain total P in this fraction. The difference between the total P and NaOH-Pi is considered to be the organic P (NaOH-Po).

The third extractant was 1 M hydrochloric acid (HCl) (Williams et al., 1971; Williams et al., 1980). No organic fraction was determined in this extract. Previous research has found negligible organic P in this extractant.

Finally, the soil sample was quantitatively transferred into a volumetric flask and digested using concentrate sulfuric acid and hydrogen peroxide (50 %) following the Hach (1988) procedure to determine recalcitrant P. This fraction is considered chemically stable and thus a less soluble P form (Hedley et al., 1982). Phosphorus

was determined in each extract and digest using the molybdate blue colorimetric method (Murphy and Riley, 1962).

Soil Mo was extracted using the diethylenetriaminepentaacetic acid (DTPA) as extracting solution (Soltanpour, 1991). This method has been used before in the extraction of Mo in soil and sediments (Tack and Veerloo, 1995). Previous studies have indicated that DTPA can be used for Mo monitoring in soils that have received biosolids (Barbarick et al., 1997; Pierzynsky and Jacobs, 1986). The DTPA extracting solution was used in a Mollisolls in Argentina for determining Mo where ICP analysis was performed as well (Lavado et al., 2000). In this experiment we used DTPA-triethanolamine (DTPA-TEA) as the extracting solution due to its buffer capacity at pH 7.3.

Molybdenum in the extract was determined using ICP-MS and selecting for ^{95}Mo isotope, which does not interfere with other isotopes (Jarvis et al., 1992). The samples were spiked and specific certified standards were used for Mo ICP-MS calibration. Sample recovery for standards was within 5% of expected values. The detection limit for the determination was 2 $\mu g\ L^{-1}$.

The general linear model (GLM) procedure of the SAS statistical program was used for the analysis of the data (SAS Institute, 1999). A probability of 0.5 or less was used to identify significant effects. Treatment means were compared using Duncan's Multiple Range procedure at a probability of 0.05 or less.

Results and Discussion

The two incubation periods, 33 and 66 days, were analyzed as two independent experiments. Control treatments with no applications are presented as a reference but were not analyzed statistically. The Webster soil description is shown in Table 1. Some important chemical properties of the P sources applied to the soils are shown in Table 2.

First experiment -incubation 33 days

Soil Molybdenum

The source of P applied (BS, SM, and TSP) caused significant differences in extractable Mo among the treatments. Extractable soil Mo was 17.2 μg kg^{-1} in BS, 10.4 μg kg^{-1} in SM and 7.9 μg kg^{-1} in TSP treatments (Table 3). Biosolids treatment increased Mo extracted from the soil the most compared with the other treatments. An increase of soil extractable Mo after BS and SM application was expected due a higher Mo content of the original source (Table 2). However, the final concentrations in all the treatments were higher than the control 7.1 μg Mo kg^{-1} (Table 3).

The initial amounts of Mo applied in each treatment were 3.5 and 14 μg in BS, 0.29 and 1.16 μg in SM, and no detectable amount in TSP treatment. The Mo recovery in the extracting solution was low in BS and SM. In BS it was 0.17 μg, and in SM it was 0.10 μg per 10-g soil.

Soil extractable Mo increased with P rate in the soil from 8.3 to 15.3 μg kg^{-1} (Table 3). The amount of Mo recovered after increasing P rate was low in BS and SM as well. Some increase of Mo concentration in soil might be due to the Mo already in BS and SM prior to application.

There was no significant difference in soil Mo extracted from any depth (Table 3). This suggests that the high soil pH had no effect on Mo solubility. We were expecting more extractable Mo at the lowest depth where pH was higher than 8 (Table 1). High soil pH has been related with high Mo solubility (Gupta, 1997). However, Goldberg et al. (1996) indicated that even though the dominant Mo adsorbing surfaces in soil are oxides, clay minerals, and organic matter. Molybdenum might be absorbed onto $CaCO_3$ at greater than pH 7.1 and be comparable in magnitude to adsorption to most clay minerals. This may explain why we did not find differences throughout soil depth at high soil pH.

Molybdenum extraction was affected by the source applied and rate of application. At a higher P rate more Mo was extracted from BS treatments than in SM and TSP treatments (Fig. 2). This suggests that the increase of Mo in BS treatments was due to the Mo contained in BS.

Soil Phosphorus Fractions

When means of sources and P application rate were compared significant differences were found in four of the six fractions of soil P. Differences were observed in the $NaHCO_3$-Pi, NaOH-Pi, NaOH-Po, and HCl-P fractions (Table 3). The only P fractions that were significantly different throughout the soil depth were the inorganic forms. The concentration of inorganic P forms was higher than the

concentration of organic forms. The total inorganic and organic P content from the BS treatment was significantly higher than those of the SM and TSP treatments (Fig. 3).

Biosolids application increased $NaHCO_3$-Pi the most, SM intermediate, and TSP the least (Table 3). This result suggests that BS contained more plant-available P forms than the other treatments. However, sometimes this fraction might represent a short-term transformed available soil P and suggests that in the absence of plants this P fraction can be transformed into other P fractions (Hedley et al., 1982). The organic fraction, $NaHCO_3$-Po, did not change due to sources applied (Table 3). The addition of the higher P rate significantly increased $NaHCO_3$-Pi concentration from 83.6 to 138.6 mg kg^{-1}. However, $NaHCO_3$-Po did not increase with the higher rate (Table 3).

Soil $NaHCO_3$-Pi concentration decreased significantly with soil depth (Table 3). This decrease may be explained by the increase of pH with depth and the presence of $CaCO_3$ (Table 1). Phosphorus solubility tends to decrease as pH increases due to reactions with Ca and Mg. Sodium bicarbonate-Po was not affected by soil depth (Table 3).

The interaction *P-source x P-rate* significantly affected the amount of $NaHCO_3$-Pi extracted. Increasing the rate of P application increased $NaHCO_3$-Pi concentration depending upon P source: BS>SM>STP (Fig. 4).

Swine manure and BS treatments contained the highest concentration of NaOH-Pi while TSP treatments the lowest (Table 3). This result is consistent with past research where BS increased NaOH-Pi (Sui et al., 1999a; Maguire, 2000). Soon and Bates (1982) suggested that this increase may be explained as an increase of Al-P and Fe-P due to the presence of significant amounts Fe and Al in the BS (Table 2)

Biosolids-treated soil had the highest NaOH-Po. The addition of BS is responsible for greater retention of P on Al and Fe sites, probably due to the significant amount of Al and Fe present in BS (Table 2) (Soon and Bates, 1982). Both NaOH-Pi and NaOH-Po increased with the addition of BS (Table 3).

The NaOH-Pi decreased with soil depth (Table 3). However, NaOH-Po was not affected by soil depth. A significant interaction was observed in source x rate in NaOH-Pi fraction. Increasing P rate resulted in a different response depending upon P source. At a higher P NaOH-Pi from TSP treatment was the lowest (Fig. 5).

The HCl-P fraction responded to the addition of BS, SM and TSP. Biosolids treatment had higher levels of HCl-P than SM and TSP treatments (Table 3). The HCl- P fraction increased with P rate (Table 3). This indicates that the soil still has capacity to form Ca-phosphates, even at the high STP levels. The HCl-P was the highest in the 0-30 cm depth and it was nearly 20 mg kg^{-1} lower in the 30-40 cm depth than the first 30 cm (Table 3). We were expecting a higher P retention at the lowest depth due to the higher soil pH and the high $CaCO_3$ content and the increase of Ca from the sources, however we did not observe it.

No responses to P source or P rate were observed in H_2SO_4-P fraction (Table 3). This suggests that most of the P content of BS, SM, and TSP was not strongly bonded onto organic and mineral surfaces.

Total P is the sum of all the fractions under consideration (Hedley et al., 1982). Biosolids and SM treatments had the highest total P content in the soil followed by TSP (Table 3). Increases in P rate resulted in an increase of the total P (Table 3). This was expected because we were adding more P to the treatments. The Sum P recovery was less with depth (Table 3). This suggests that P was not totally extracted by our procedure under such conditions. Total P analysis indicates an average mass balance close to 652 mg kg^{-1} in all treatments (Table 3).

Second experiment incubation 66 days

Soil Molybdenum

The application of P sources resulted in significant differences in the extractable Mo among the treatments. Extractable Mo was 25.8 in BS treatments 13.8 in SM treatments, and 7.4 µg kg^{-1} in TSP treatments (Table 4). We observed that the amount of Mo extracted after 66 days was higher than after 33 days of incubation, we did not observe any increase with the control treatments. Significant differences in BS but not in SM and TSP were observed (Table 3, 4). Increasing the P rate increased extractable soil Mo concentration from 11.1 to 20.3 µg kg^{-1} (Table 4).

Soil Mo concentration was not affected by soil conditions throughout soil depth (Table 4). The interaction *P-source* and *P-rate* was significant. Increasing the P rate increased Mo concentration more in BS than in SM and STP treatments (Fig. 6). This result suggests that the increase in soil extractable Mo at the high P rate was caused by the Mo in BS and not by the higher P rate.

Soil Phosphorus Fractions

Significant differences were found in three of the six fractions of soil P when means of sources and P application rate were compared. Differences were observed in $NaHCO_3$-Pi, NaOH-Pi, and HCl-P (Table 4). The inorganic P fractions were significantly different throughout the soil depths, while the only organic fraction that had differences was NaOH-Po. The organic fraction represented more than 40% of total extractable P in the treatments (Table 4).

The inorganic P fraction concentrations were higher than the organic forms. The organic P forms were significantly higher after 66 days of incubation than at 33 days (Fig. 3, 7). The inorganic soil P fraction was significantly higher in BS and SM than in TSP. This suggests that in 66 days part of the organic P fraction was mineralized into the inorganic fraction.

Biosolids application resulted in the highest $NaHCO_3$-Pi fraction (128.2 mg kg^{-1}) and TSP treatments the lowest (93.5 mg kg^{-1}) among all sources. The addition of the high P rate significantly increased $NaHCO_3$-Pi (Table 4). The $NaHCO_3$-Pi concentration decreased with soil depth, suggesting that labile P decreases with higher pH and higher $CaCO_3$ content. The interaction between *P-source x -Prate* was statistically significant, which suggests that increase of P rate increases

$NaHCO_3Pi$ concentration but differentially depending on P source: BS>SM>STP (Fig. 8). No response was observed in the organic fraction to the addition of treatments (Table 4).

Swine manure and BS treatments had the highest amount of NaOH-Pi whereas TSP had the lowest (Table 4). The NaOH-Po was not affected by the treatments (Table 4). Increasing P rate significantly increased the concentration of mean NaOH-Pi from 57.5 to 72.7 mg kg^{-1} (Table 4). This difference suggests that the addition of these sources enhanced the amount of P associated with Al and Fe.

The NaOH-Pi fraction decreased with soil depth (Table 4). These results suggest a possible lower content of Al and Fe sorption with depth, which is consistent with high pH and $CaCO_3$ content. The NaOH-Po fraction was least in the 30-40 cm soil depth (Table 4). The $CaCO_3$ content at this depth was greater than 5% and pH is higher than 8, conditions that probably enhance Ca-P bonding (Table 1).

The *P-source x P-rate* interaction was significant for both NaOH-Pi and NaOH-Po (Figs 9,10). This indicates that increasing the P rate produced different NaOH-Pi and NaOH-Po content, depending upon P source. In SM and TSP the change of rate caused little change in either NaOH-Pi or NaOH-Po fractions. Biosolids treatment caused a significant increase in these fractions.

Biosolids- and SM- treated soils had higher HCl-P fractions than TSP (216.7, 219.3, and 200.1 mg kg^{-1}, respectively) (Table 4). This fraction is associated with occluded P and apatite-type minerals. Increasing P rate increased the amount of the HCl-P fraction (Table 4). Soil depth affected HCl-P fraction; more P was extracted from the two top depths than the two lower depths (Table 4). The *P-*

source x P-rate interaction was significant for HCl-P. Increasing P rate increased the HCl-P fraction depending on the source: BS>SM>STP (Fig. 11). This result is consistent with the amount of Ca present in the sources and suggests that BS and SM enhanced the formation of Ca-phosphates (Table 2).

No differences in the H_2SO_4-P fraction were observed due to the treatments (Table 4).

Increasing the P rate resulted in an increase of the Sum-P recovered regardless of the P source (Table 4). Increasing P rate resulted in a high Sum-P (Table 4). We were expecting to recover more P where we applied a higher amount. The Sum-P content decreased at the lower two depths (Table 4). A significant *P-source x P-rate* interaction was observed. At the higher P rate the higher the total P was in BS than SM and TSP (Fig 12). The amount of total P recover was within 50 g kg^{-1} in all the treatments (Table 4).

Summary and Conclusions

The application of BS and SM increased extractable soil Mo more than the application of TSP. Biosolids and SM application increased extractable Mo after 66 days of soil incubation. However, extractable Mo was not affected by the application of TSP. Consequently, the addition of BS and SM containing Mo may enhance Mo availability in soils. Extractable Mo was dependent on the source applied, but not on P rate of application. Both BS and SM contained Mo.

The application of BS, SM, and TSP to high STP soil resulted in differences in extractable P fractions in the soil. The proportion of soil P fractions was: NaOH-Po > HCl-P > $NaHCO_3$-Pi > H_2SO_4-P. The $NaHCO_3$-Pi, NaOH-Pi and HCl-P fractions increased in BS treatments the most. This suggests that BS have a potential to increase other P fractions due to the addition of Al and Fe associated to P sorption. Swine manure and BS increased the extracted HCl-P suggesting that these sources may enhance Ca-P bonding.

Most of the soil P fractions were affected by the *P-source x P-rate* interaction. This indicates that an increase of P rate affected the P fractions differentially, depending upon the source. The BS treatments, in general, contained more P in all fractions than the other sources at the higher P application rate. Extractable P fractions were affected by soil depth. The $NaHCO_3$-Pi fraction was less at lower depths than surface depths, due to differences in pH, and initial P concentration, the lower depth probably had a greater capacity to bond labile P.

The application of BS, SM, and TSP to a high STP soil resulted in changes in all the soil P extractable fractions. Biosolids increased the labile P, the Fe-Al-P, and the Ca fractions, and BS the Fe-Al-P, and the Ca fractions. However, the changes in the soil P fractions did not result in changes in soil Mo concentration.

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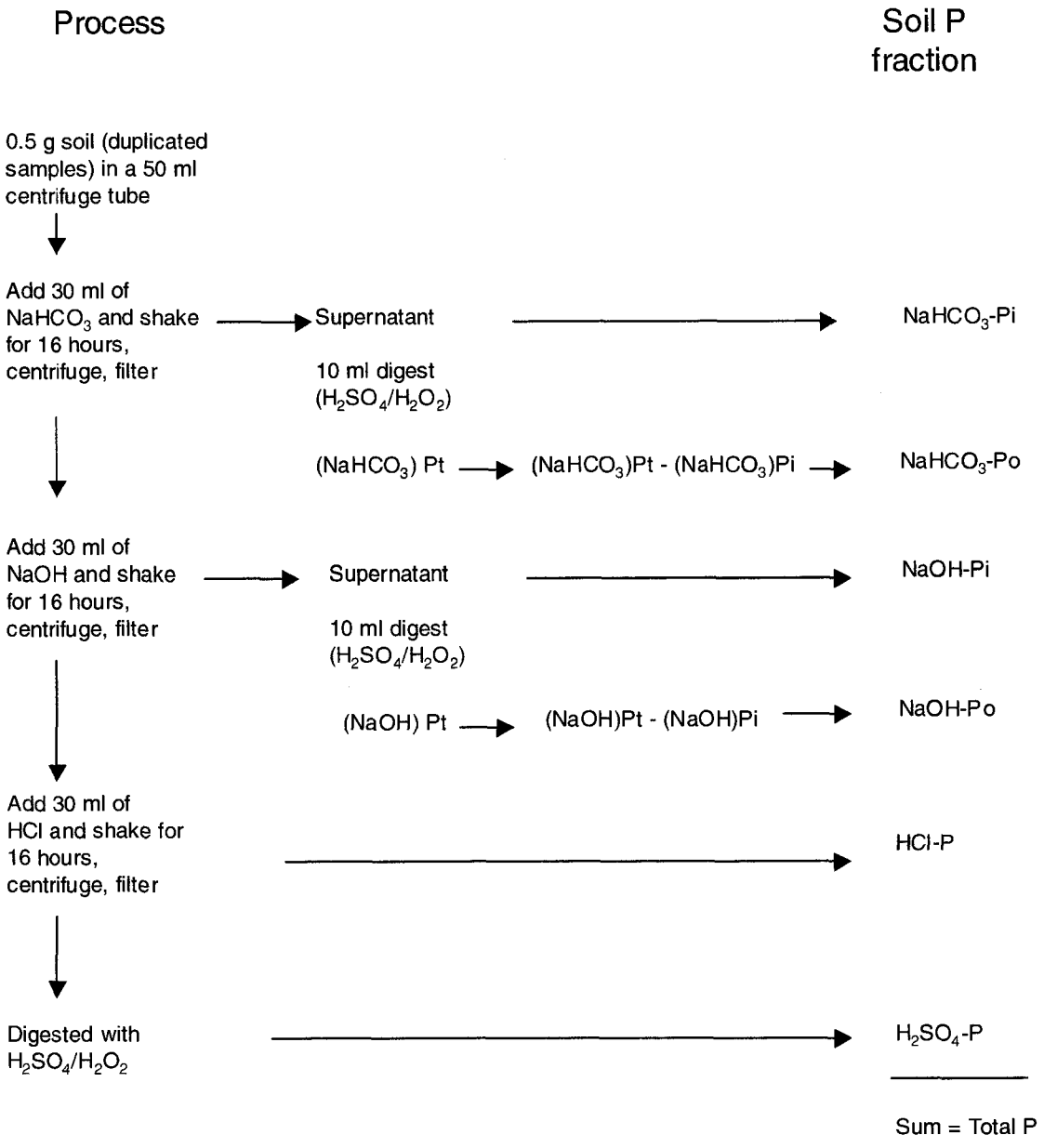

Figure 1. Sequential P fractionation scheme. A modified method from Hedley et al. (1982).

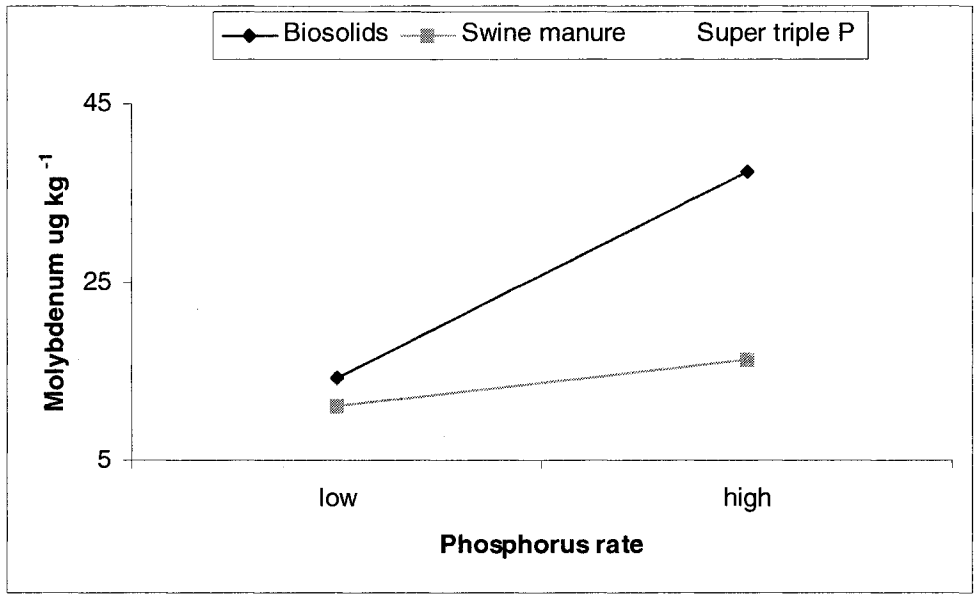

Figure 2. DTPA-TEA extractable molybdenum in soils treated with biosolids, swine manure and triple superphosphate at twophosphorus rates and incubated for 33 days.

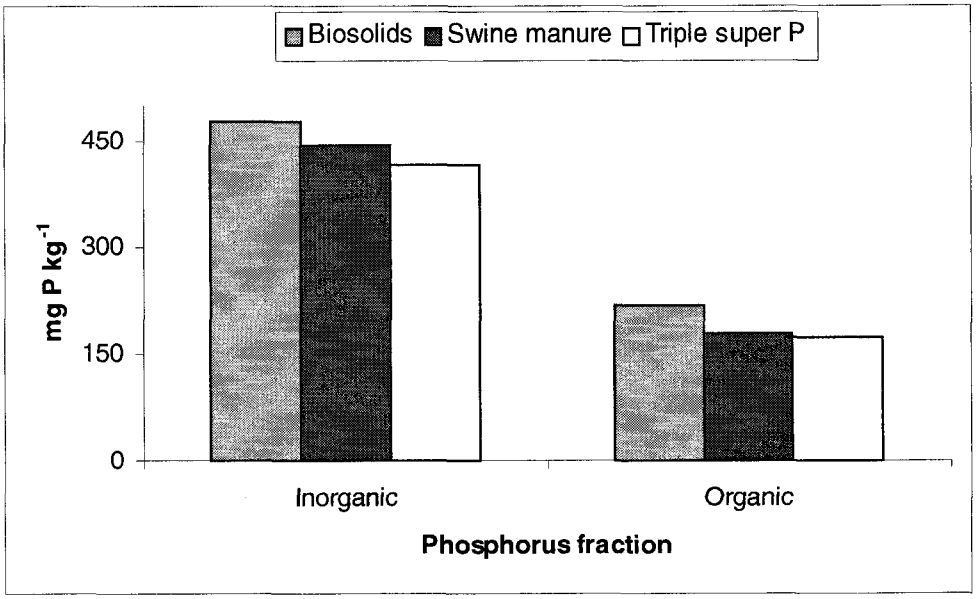

Figure 3. Absolute amounts of inorganic ($NaHCO_3$+ NaOH + HCl + H_2SO_4/H_2O_2) and organic ($NaHCO_3$ + NaOH) phosphorus soil fractions after 33 days of incubation.

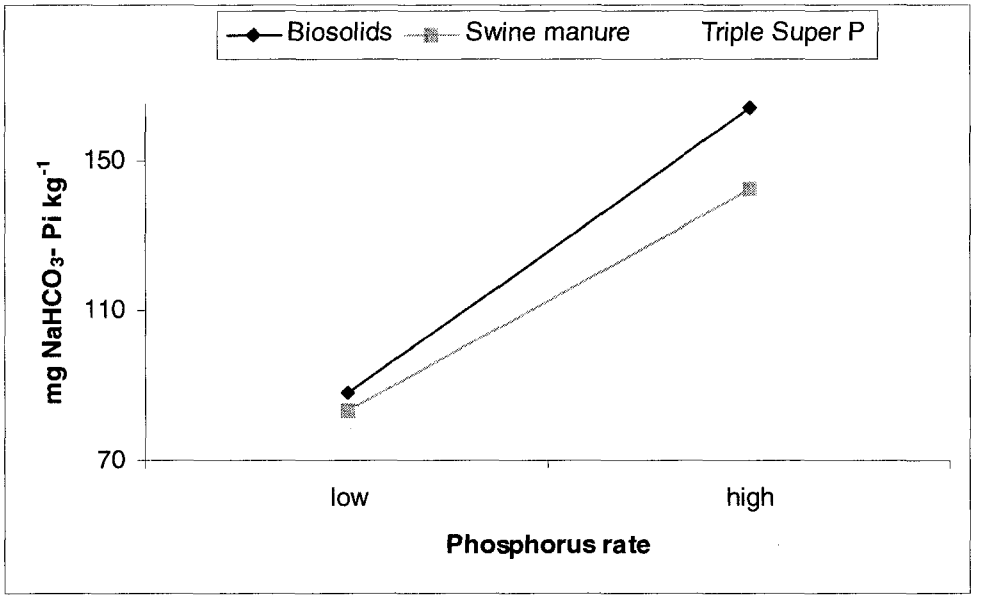

Figure 4. Extractable $NaHCO_3$-Pi in soils treated with biosolids, swine manure, and triple superphosphate at two phosphorus rates after for 33 days of incubation.

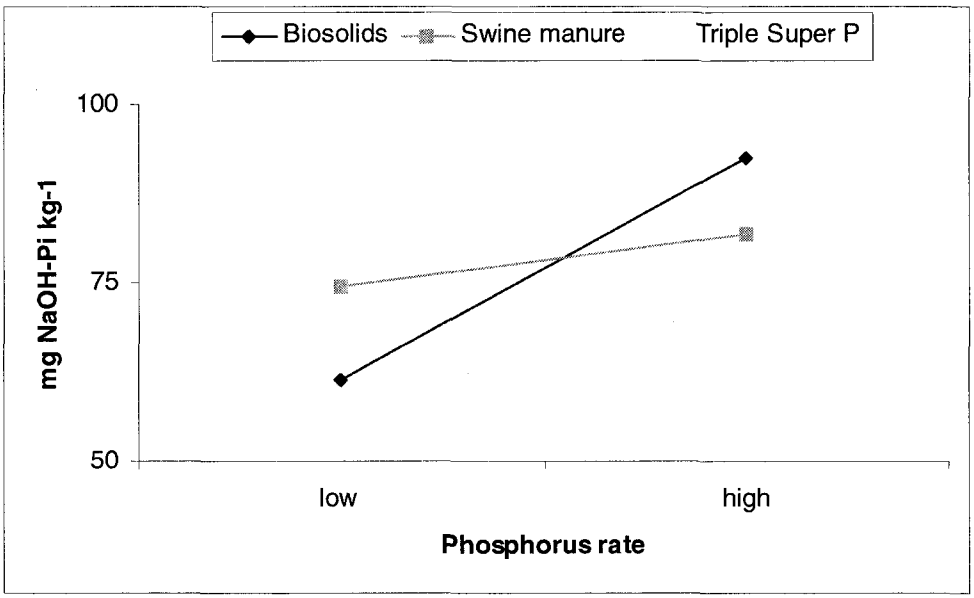

Figure 5. Extractable NaOH-Pi in soils treated with biosolids, swine manure, and triple superphosphate at two phosphorus rates after 33 days of incubation.

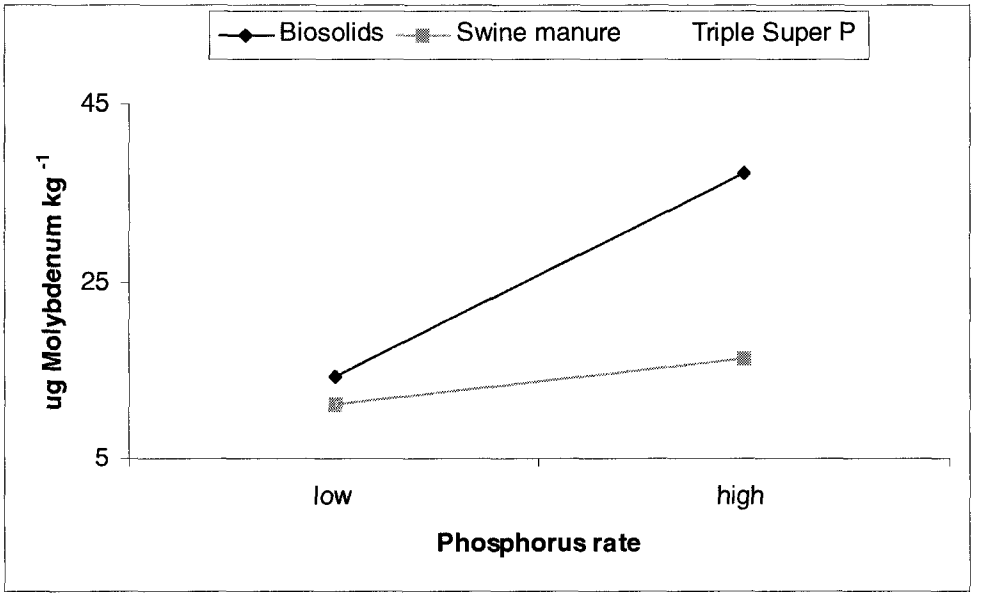

Figure 6. Extractable Mo in soils treated with biosolids, swine manure and triple superphosphate at two phosphorus rates after 66 days of incubation.

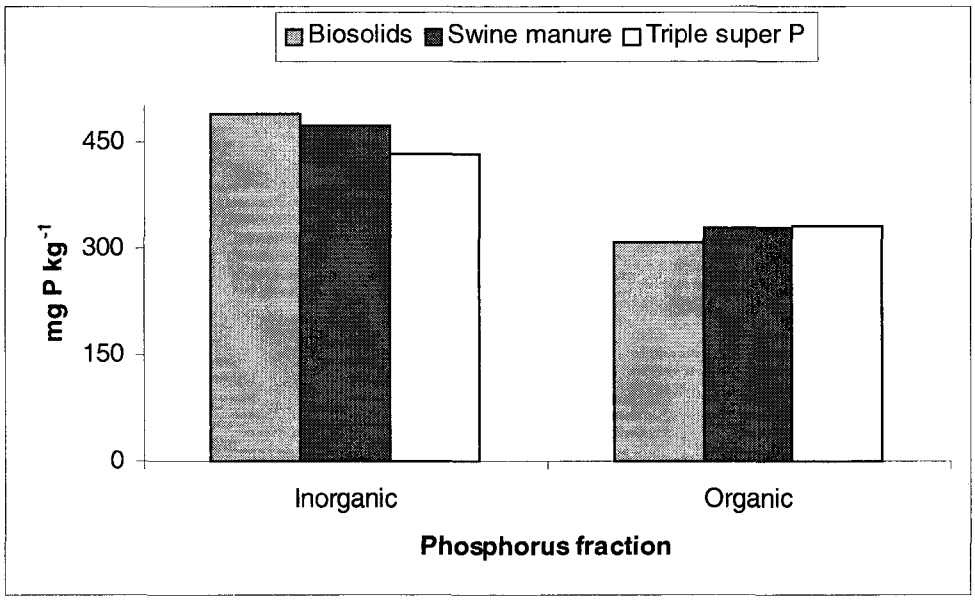

Figure 7. Absolute amounts of inorganic ($NaHCO_3$+ NaOH + HCl + H_2SO_4/H_2O_2) and organic ($NaHCO_3$ + NaOH) phosphorus soil fractions after 66 of days incubation.

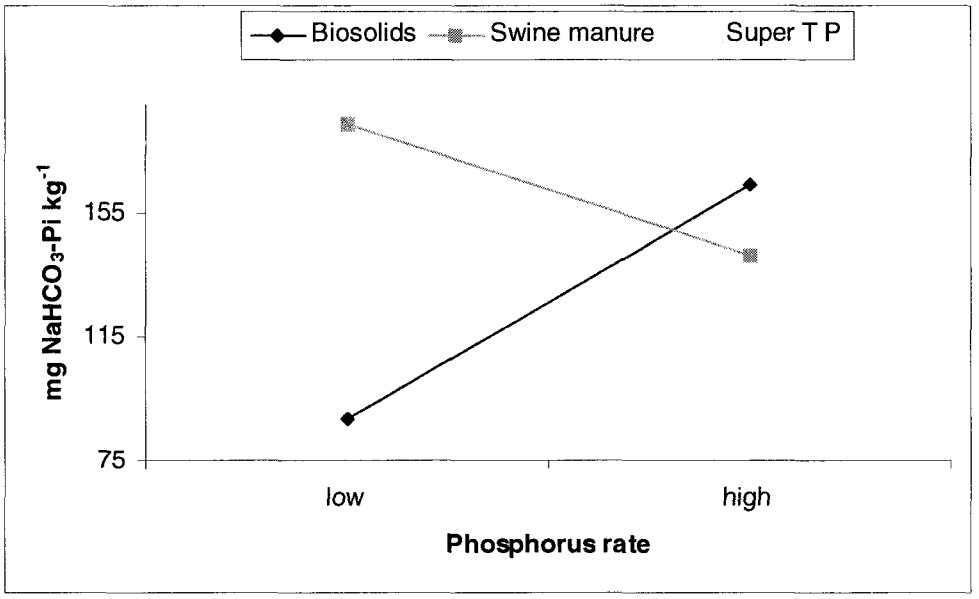

Figure 8. Extractable $NaHCO_3$-Pi in soils treated with biosolids, swine manure, and triple superphosphate at two phosphorus rates and incubated for 66 days.

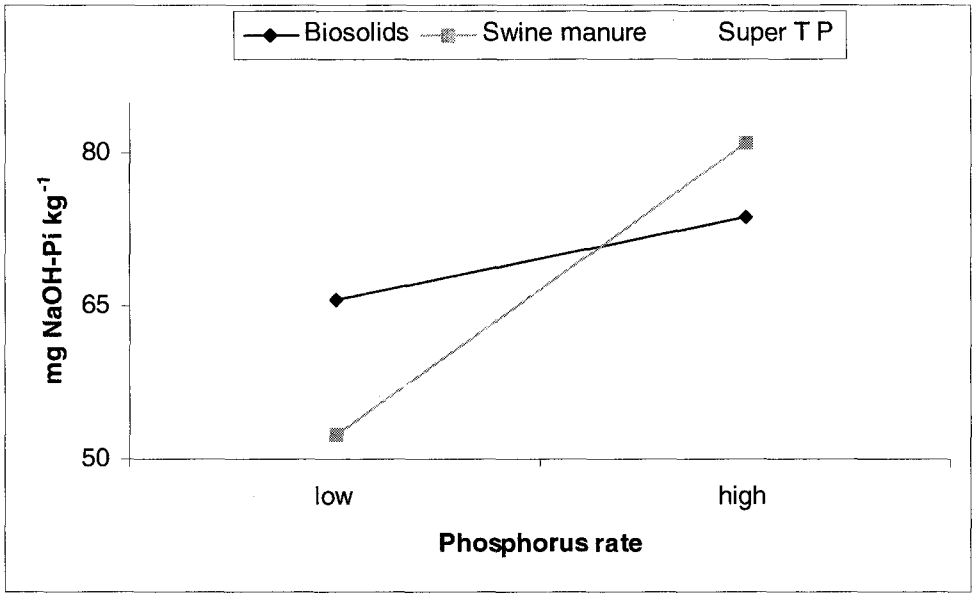

Figure 9. Extractable NaOH-Pi in soils treated with biosolids, swine manure, and triple superphosphate at two phosphorus rates and incubated for 66 days

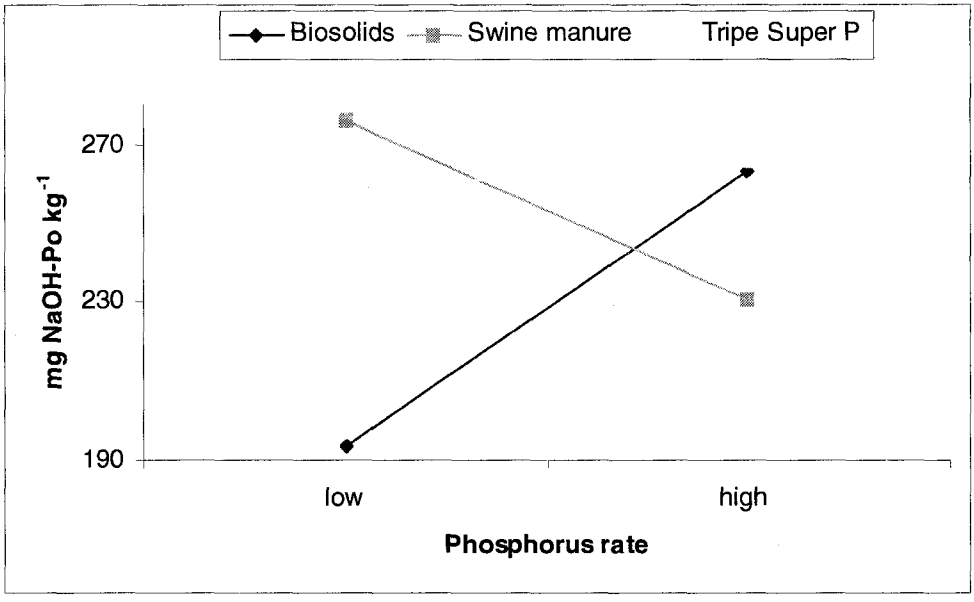

Figure 10. Extractable NaOH-Po in soils treated with biosolids, swine manure, and triple superphosphate at two phosphorus rates and incubated for 66 days.

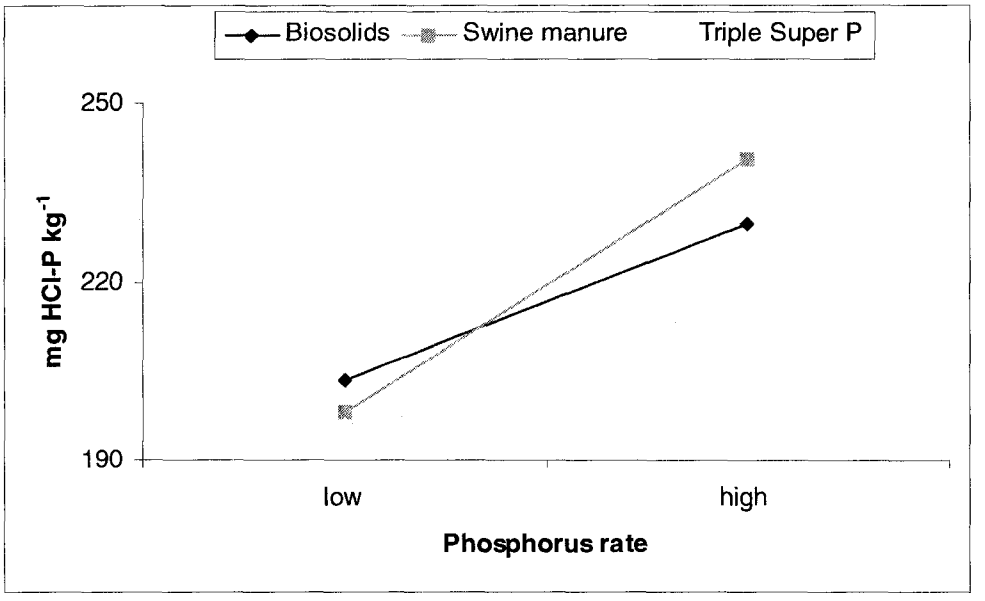

Figure 11. Extractable HCl-Pi in soils treated with biosolids, swine manure, and triple superphosphate at two phosphorus rates and incubated for 66 days.

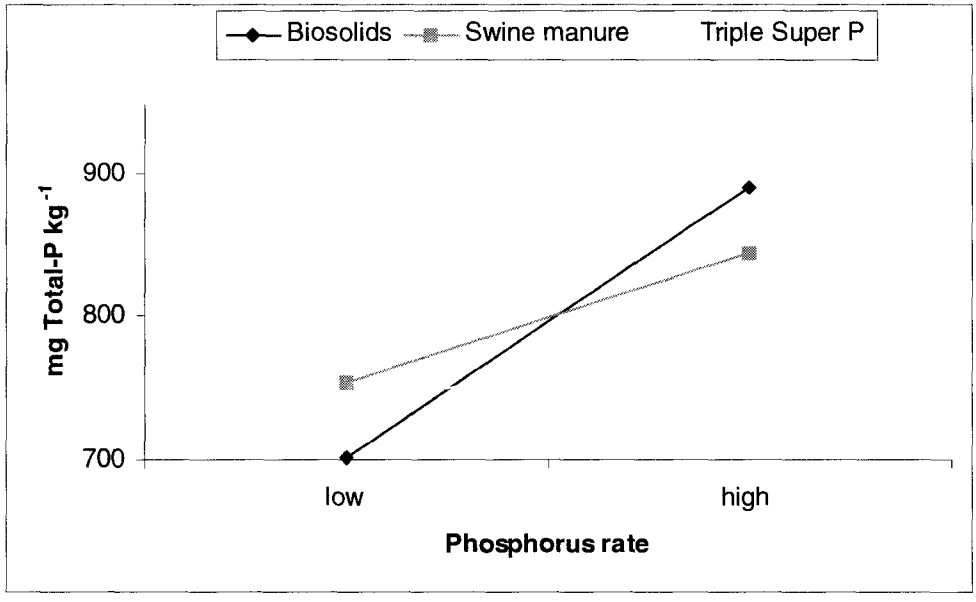

Figure 12. Total-P in soils treated with biosolids, swine manure, and triple superphosphate at two phosphorus rates and incubated for 66 days.

Table 1. Selected soil chemical properties at four depths content in a Webster soil prior to incubation.

		Phosphorus			
Soil	**pH**	**Total**	**Olsen**	**$CaCO_3$**	**TOC [1]**
depth (cm)		mg kg^{-1}		g kg^{-1}	
0 - 10	7.2	586	27.0	nd [2]	27
10 - 20	7.4	576	13.0	2	26
20 - 30	7.5	447	8.0	nd	25
30 - 40	8.1	485	5.0	53	23

[1] Organic carbon
[2] No detectable level

Table 2. Selected chemical properties of biosolids and swine manure applied to a Webster soil prior to incubation.

	Biosolids	**Swine manure**
Total solids (g kg^{-1})	23.6	12.1
Total N (g kg^{-1}) *	2.6	3.6
Total P (g kg^{-1}) *	12	8
Total Ca (g kg^{-1}) *	230	84
Total Fe (mg kg^{-1}) *	8536	730
Total Al (mg kg^{-1}) *	2850	3900
Total Mo (mg kg^{-1}) *	14.1	0.8

* wet basis

Table 3. Soil extractable molybdenum and phosphorus soil fractions after biosolids (BS), swine manure (SM), and triple superphosphate (TSP) were applied at a low and a high rate to samples from four depths of a Webster soil and incubated for 33 days.

	Molybdenum	Phosphorus							
	DTPA-TEA	$NaHCO_3$		NaOH		HCl	H_2SO_4/H_2O_2	Sum	Total
		inorganic	organic	inorganic	organic				
	$\mu g\ kg^{-1}$	$mg\ kg^{-1}$							
source									
BS	17.2 b	125.8 c	80.5	75.7 b	135.8 b	199.6 b	76.7	694.1 c	696.4
SM	10.4 a	112.8 b	72.8	77.9 b	104.1 a	173.3 a	79.5	630.6 b	668.8
TSP	7.9 a	93.5 a	79.6	64.8 a	120.7 a	179.3 a	76.7	619.6 a	647.9
p>F	***	***	ns	***	***	***	ns	***	ns
rate									
low	8.3 a	83.6 a	71.4	64.5 a	105.2 a	169.8 a	77.8	572.2 a	588.7 a
high	15.3 b	138.6 b	76.7	81.8 b	123.2 b	198.3 b	77.5	695.4 b	679.4 b
p>F	***	***	ns	***	*	***	ns	***	***
0	7.1	61.8	79.5	59.8	117.1	160.1	74.4	552.7	547.5
depth (cm)									
0 - 10	11.6	136.4 d	70.6	85.4d	112.0	190.6 b	77.4	673.3 c	666.5
10 - 20	11.1	121.8 c	73.8	80.5 c	114.8	195.2 b	78.3	666.2 c	671.2
20 - 30	11.9	99.7 b	71.0	69.5 b	117.9	185.6 b	77.1	620.7 b	645.6
30 - 40	12.6	83.6 a	80.7	57.2 a	112.1	164.7 a	77.6	576.0 a	628.9
p>F	ns	***	ns	***	ns	***	ns	***	ns

ns = non significant, * = significant at 0.05 level, ** = significant at 0.01 probability level, *** = significant at 0.001 or lower probability level.

‡ numbers in columns followed by different letters are significantly different (P>0.05).

Table 4. Soil extractable molybdenum and phosphorus soil fractions after biosolids (BS), swine manure (SM), and triple superphosphate (TSP) were applied at a low and a high rate to four depths of a Webster soil 3 and incubated for 66 days.

	Molybdenum	*Phosphorus*							
	DTPA-TEA	*$NaHCO_3$*		*NaOH*		*HCl*	*H_2SO_4/H_2O_2*	*Sum*	*Total*
		inorganic	*organic*	*inorganic*	*organic*				
	µg kg^{-1}	*mg kg^{-1}*							
source									
BS	25.8 c	128.2 **c**	80.6	69.7 **b**	138.4	216.7 **b**	74.6	708.2	698.2
SM	13.8 b	111.1 **b**	72.9	66.7 **b**	153.0	219.3 **b**	74.0	652.6	699.0
TSP	7.4 a	93.5 **a**	68.6	62.0 **a**	162.1	200.1 **a**	76.2	662.5	688.7
p>F	***	***	ns	**	ns	***	ns	ns	ns
rate									
low	11.1 a	73.6 **a**	71.4	57.5 **a**	132.5	199.4 **a**	76.2	610.5 **a**	605.1**a**
high	20.3 b	107.6 **b**	76.7	72.7 **b**	140.3	224.8 **b**	73.3	695.4 **b**	688.1 **b**
p>F	***	***	ns	***	ns	***	ns	***	*
0	6.8	50.8	76.1	56.8	147.1	160.1	74.4	565.1	576.1
depth (cm)									
0 -- 10	15.9	138.4 **d**	70.6	89.2 **d**	136.9 **b**	217.3 **a**	74.0	726.4 b	699.2
10 -- 20	15.0	121.8 **c**	73.8	73.7 **c**	150.3 **b**	221.5 **a**	74.3	717.2 b	701.1
20 -- 30	15.7	99.7 **b**	71.0	59.2 **b**	136.2 **b**	206.2 **a**	75.0	747.2 a	706.2
30 -- 40	16.1	83.6 **a**	80.7	42.4 **a**	118.3 **a**	243.2 **b**	76.3	644.5 a	688.6
p>F	ns	***	ns	***	*	***	ns	***	ns

ns = non significant, * = significant at 0.05 level, ** = significant at 0.01 probability level, *** = significant at 0.001 or lower probability level.

‡ numbers in columns followed by different letters are significantly different (P>0.05).

CHAPTER 3. THE FATE OF PHOSPHORUS FOLLOWING THE APPLICATION OF BIOSOLIDS, SWINE MANURE, AND TRIPLE SUPERPHOSPHATE TO A WEBSTER SOIL IN IOWA.

A paper prepared for submission to the Environmental Soil Quality Journal

J. D. Hernandez* and R. Killorn **

Abstract

The possible effects of the application of biosolids (BS) and swine manure (SM) to high phosphorus (P) test soils has been widely debated due to the potential increase in P pollution. The application of these materials to soils might result in changes in water, soil, and crop quality. Increasing P in an already high soil-test P (STP) soil may result in changing P dynamics in agro-ecosystems and enhancing P movement away from sorption sites. The purpose of this study was to determine the effect of BS, SM, and triple superphosphate (TSP) applications on the soil P content at four depths of a Webster soil. A field study was conducted where BS, SM and TSP were applied at three rates to a high STP soil, with pH > 6.0. Soybean (*Glycine max*) and corn (*Zea mays*) were planted in plots A and B, respectively, in 2001 and the following year the crops were rotated. Soil samples were collected from the plots three weeks after treatment application (t1) and following harvest (t2). The soil samples were collected in 10 cm increments to a depth of 40 cm. Soil samples were analyzed for P (Olsen and $CaCl_2$) and pH. In 2001, and 2002, TSP increased soil Olsen-P concentration the most in all plots. Treatments did not affect $CaCl_2$-P in either plot in 2001. Increasing P rate resulted in increasing soil P only in the top

* Hernandez, J. D. Research Assistant. Dept. Agronomy, Iowa State University. Ames, IA 50011
** Killorn, R. Professor. Dept. Agronomy, Iowa State University, Ames IA, 50011

10-cm soil depth at t2 in 2002. Soil pH was not affected by treatments.

Introduction

The use of BS and SM as sources of nutrients for crop production is a practice that is currently in use, more as a way of disposing of waste than for its efficient utilization as source of nutrients. Biosolids and SM have been used as sources of N and P for years, however, there is very little information regarding the proportions and amounts that can be used by crops and their consequences in the soil-crop system (Frossard et al., 1996).

Phosphorus is considered a major factor in increasing water quality problems (Burkeholder and Glasgow, 1997). Due to the low mobility of P in soils and the high P-fixation capacity of most soils, movement of P through the profile has been considered irrelevant (Eghball et al., 1990). However, continuous increases of P content of already high STP soils have been shown to cause P accumulation in the soil surface, soil solution, and runoff water (Heckrath et al., 1995; Sui et al., 1999). Also continuous application of P in BS might increase the movement of P, particularly in high P test soils (Sharpley et al., 1984; Sui and Thompson, 2000).

Several studies have shown that the use of BS in crop production has minimal effect on agricultural ecosystems (Phillips and Grant, 1994) when applied at appropriate rates. However, repeated manure application to high STP soils might increase P mobility in the soil (Gerritse et al., 1982; Chang et al., 1991; James et al., 1996; White and Sharpley, 1996).

Summers et al. (1979) observed minimal P leaching in a study in Pennsylvania. Other studies have shown that continuous application of BS will result in a build up of P in soil profiles (Peterson et al., 1994; Sui et al., 1999). The same will happen with SM (Eghball et al., 1990). An increase of soil P above concentrations required for crop production is a concern due to the potential for environmental degradation (Burkholder and Glasgow, 1997). Additionally, increasing P in soil solution may cause interactions with other nutrients that may affect the agroecosystem.

Increasing the amount of P dissolved in the soil solution might cause a decrease of P from sorption sites in soil already high in P. Under repeated manure application soil has shown the potential for P leaching (Chang et al., 1991; James et al., 1996). Sui and Thompson (2000), in a laboratory investigation, found that the application of BS to high STP soil increased the P concentration in the soil solution, suggesting a decreased ability of the soil to sorb P. Biosolids and SM applications might increase the movement of P in high P-test-soils. Eghball et al. (1996) found that when animal manure was applied P moved deeper in the soil profile than when inorganic fertilizers were applied at similar P rates.

The effect of increasing soluble phosphate on soil P movement in high STP soils needs to be investigated. This information is important not only from an environmental point of view, but also due to the interaction of P with other nutrients. The purpose of this study was to assess the effect of BS, SM, and TSP applied at three P rates on changes in soil P content at four depths in a high STP soil in Iowa.

Materials and Methods

The experiment was conducted at the Iowa State University (ISU), Agronomy Farm, where traditional tillage was used in soybean and corn production. The soil was a Webster soil (Fine-loamy, mixed, superactive, mesic Typic Endoaquolls), with organic matter (OM) content of 3.6%, pH (Thomas, 1996) and P (Olsen et al., 1954) and P ($CaCl_2$) (Self-Davis et al., 2000) shown in Table 1.

Biosolids, SM, (Table 2) and TSP (0-45-0) were applied to the field at three rates to supply 15, 30 and 60 kg P ha^{-1}. The rate calculation was based on total P in BS, SM and TSP. Swine manure was obtained from the ISU Swine Nutrition Farm and BS from the Water Pollution Control Facility, Ames, Iowa with Mo concentration of 0.6 and 13 mg kg^{-1}, respectively. Ammonium nitrate (NH_4NO_3) was applied in corn plots to equalize the amount of N considering initial N credits from SM and BS and a target rate of 120 kg ha^{-1} N. It was assumed 500 g kg^{-1} of plant available N from both BS and SM.

The field was divided into two plots, A and B, then each of those was subdivided into 30 subplots 4 m long x 5 m wide. Swine manure, BS, and TSP were initially manually broadcast and then incorporated with a cultivator. Ten days after the treatments were applied corn (Pioneer 35P12) and soybean (Pioneer 92B62) were planted in plot A and plot B, respectively. Corn was planted at 79,000 plants ha^{-1} and soybean at 340,000 plants ha^{-1}. This experiment was conducted for two soybean-corn cycles in the same area.

Soil samples were taken at 0-10, 10-20, 20-30 and 30-40 cm depth 21 days after treatment application (t1), and after harvest (t2). The soil analyses included pH in 0.01 M $CaCl_2$ (Thomas, 1996) and sodium bicarbonate extractable P (Olsen et al., 1954) at t1 and t2 and P extracted with 0. 01 M $CaCl_2$ only at t2 (Self-Davis et al., 2000). Phosphorus in the extracts was determined using the molybdate blue colorimetric method of Murphy and Riley (1962).

Data for each year were analyzed as separate experiments. The experimental design was a randomized complete block, with a factorial treatment arrangement, with 2 factors, P source and P rate and 3 replicates. The soil P content using both extractants and pH were analyzed by using analysis of variance (ANOVA). Analysis of variance was performed using the general linear model (GLM) procedure of the SAS statistical program (SAS Institute, 1999). A probability of 0.05 or less was used to declare significance. Means of the treatments were compared using Duncan's Multiple Range procedure at a probability level of 0.05.

Results and Discussion

The 2001 and 2002 data were analyzed and interpreted as two separate experiments. Control treatments with no applications are presented for reference, but were not analyzed statistically. The Olsen-P content of the surface 10 cm of soil was 27 mg kg^{-1} (Table 1), which is considered to be high for corn and soybean production in Iowa (Voss et al., 1996). The DTPA-TEA extractable Mo content throughout 40 cm was 6 μg kg^{-1}. Some soil and P source characteristics are presented in Tables 1 and 2.

Soil Phosphorus 2001

Soil test P increased similarly regardless of the source in the top 10 cm of plots A and B at t1 (Table 3). This was expected because similar rates of P were applied. Higher accumulations than t1 of Olsen P were observed in all treatments at t2 for both plots, and the Olsen-P concentrations in TSP treatments were higher than SM and BS (Table 3). Our results suggest that Olsen-extractable P was higher in TSP treatments than the other sources. However, the Olsen-P extraction without any further digestion and following colorimetric determination will not detect all the organic P. A total total acid/base digestion should be performed to count for this difference.

In 2001, at t2, significant differences were observed throughout the 40 cm depth in plot A. In plot B, TSP treatments significantly increased soil P in only the top 20 cm (Table 3). This suggests that the crop type may play a role in the mobility and treatment effect on Olsen P throughout the soil profile. In the soybean plot (A), P concentration increased throughout the soil profile and this increase was bigger than

the corn plot (B). McCoy et al. (1986) found that P from TSP was three to seven times more available to plants than P from BS. They attributed this response in part to the Al and Fe content of the BS, and its capacity to bond with P in solution.

Conversely, other studies have indicated repeated SM and BS applications to high STP soils increased soil extractable P in comparison with inorganic sources (Meek et al. 1979; Eghball et al., 1990; James et al., 1996). This appears to be primarily due to aneventual soil P saturation and possibly to ion competition of inorganic and inorganic products found in SM and BS for P sorption sites (Chang et al., 1991, James et al., 1996, White and Sharpley, 1996; Sui and Thompson, 2000). Meek et al (1979) found that repeated manure application on farm soils increased Olsen-P throughout a 30-cm depth, and the P content was always higher than where mineral P fertilizers had been applied. Malhi et al. (1992) found no mobile P throughout a soil profile due to the application of TSP.

The rate of P application did not significantly affect the extractable Olsen-P (Table 3). The low mobility of P in the soil may justify this response at t1. However, P concentration did not respond to increasing P rate even at t2. This suggests that this soil had a high capacity to sorb P. Additionally, this result might indicate that P saturation was not reached even at the high P application rate. Meek et al. (1979) found that increasing P rate application from SM resulted in a dramatic increase in Olsen-P in comparison with inorganic fertilizer in the first 30 cm. We did not observe this result in our experiment.

The application of the treatments in plot A and B resulted in no significant differences in the $CaCl_2$-P in 2001 (Table 3).

Soil Phosphorus 2002

Application of P sources resulted in significant differences among treatments in plot A in the first 30 cm of soil at t1 (Table 4). The TSP treatment had more Olsen-P than any other sources in the top 20 cm of soil and averaged almost 50% more Olsen-P than BS in SM the top10 cm depth. No differences were observed due to P source below the 30 cm depth (Table 4). In t2, TSP treatments resulted in nearly 20 mg kg^{-1} more P than BS and SM in the top 10 cm (Table 4). Even though there was an increase of P in the 10-20 cm depth in 2002 depth in comparison with 2001, all the sources increased Olsen-P similarly (Table 4). In plot B, the addition of P sources resulted in more Olsen-P in TSP and SM treatments than BS the top 20 cm at t1 (Table 4). At t2, Olsen P increased, and there were significant differences among the treatments in the first 30 cm. Triple superphosphate had the highest P concentration (Table 4).

The rate of P application did not significantly change soil Olsen-P at t1 in either plot. However, P concentration increased significantly at t2 in both plots in the top 10 cm of the soil. This increase in soil Olsen-P was only significant at an application rate of 60 kg P ha^{-1} (Table 4).

Triple superphosphate treatments contained more than 3.0 mg kg^{-1} extractable $CaCl_2$-P than SM and BS treatments in plot A (Table 4), suggesting a higher P concentration in the soil solution using TSP than BS and SM. In plot B the $CaCl_2$-P was not affected by P source (Table 4). Increasing P rate did not result changes in $CaCl_2$-P in plot A. However, in plot B, 60 kg P ha^{-1} treatment contained

the highest $CaCl_2$-P (Table 3). This suggests that the crop history might play a role in the $CaCl_2$-P extracted from the soil at higher P rates.

Soil pH

In 2001, the averages of soil pH at the first 10 cm of soil depth in plot A and B in both plots were 6.81 for TSP, 6.60 for SM, and 6.59 for BS. In 2002, soil average pH was 6.79 for TSP, 6.56 for SM, and 6.56 for BS. We were expecting increase in the soil pH after using for two years BS. Pierzynsky and Jacob (1986) reported increases in soil pH after application of BS on soils cultivated with corn and soybean. However, soil pH in our study was not affected by the treatments at any depth either year .

Summary and Conclusions

In high STP soils, no differences in Olsen-P content were observed three weeks after application of P sources in 2001. However, TSP increased Olsen-P more than BS and SM throughout the 40-cm of soil profile at harvest in the soybean plot A, and 20-cm in corn plot B in 2001. In 2002, at t1 and t2 TSP increased Olsen-P the most throughout 20 and 30 cm depth in the soybean plot. Meanwhile, at harvest the amount of P-Olsen was similar in all the sources below 10-cm depth in plot A.

Increasing P rate did not change soil Olsen-P concentration in 2001. However, in 2002, increasing P rate resulted in more Olsen-P concentration in the top 10-cm of soil at t2 in both plots.

Triple superphosphate treatments increased extractable $CaCl_2$-P more than SM and BS treatments in plot A in 2001 and in 2002. In plot B, TSP treatments resulted in more $CaCl_2$-P than BS only in 2001.

Increasing P rate did not result in changes in $CaCl_2$-P in either plot in 2001. However, in plot B, 60 kg P ha^{-1} treatment resulted in more $CaCl_2$-P than the lower P rates. This suggests that the crop history might play a role in the $CaCl_2$-P extracted from the soil at higher P rates.

The application of BS, SM, and TSP resulted in changes and increases in soil P content. The changes were more attributed to the P sources than to the P rate. Triple super phosphate increased soil P the most throughout the four soil depths in this high STP soil in Iowa. Increasing P rate increased only Olsen P in the top 10 cm of soil the second year of the experiment.

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Table 1. Selected chemical characteristics of the Webster soil used in this study.

Soil	pH	Phosphorus			$CaCO_3$
		Olsen	$CaCl_2$	Total	
		mg kg^{-1}			g kg^{-1}
depth (cm)					
0 - 10	6.9	27.0	2.1	586	0
10 - 20	6.3	13.0	0.7	576	2
20 - 30	6.1	8.0	0.6	447	0
30 - 40	6.0	5.0	0.1	485	1

Table 2. Selected chemical characteristics of the P sources biosolids (BS), swine manure (SM) used in this study.

	Biosolids	**Swine manure**
Total solids (g kg^{-1})	23.6	12.1
Total N (g kg^{-1}) *	2.6	3.6
Total P (g kg^{-1}) *	12	8
Total Ca (g kg^{-1}) *	230	84
Total Fe (mg kg^{-1}) *	8536	730
Total Al (mg kg^{-1}) *	2850	3900
Total Mo (mg kg^{-1}) *	14.1	0.8

* wet basis

Table 3. Soil Phosphorus (Olsen and $CaCl_2$) content in 0-10, 10-20, 20-30 and 30-40 cm soil depths three weeks after planting corn and soybean (t1) and at harvest (t2) following biosolids (BS), swine manure (SM) and triple superphosphate (TSP) applications at three P rates to a Webster soil in 2001.

	Phosphorus *(mg kg^{-1})*									
	Olsen									**$CaCl_2$**
	t1					t2				
	0 -10	10 - 20	20 - 30	30 - 40		0 -10	10 - 20	20 - 30	30 - 40	0-10
	cm					cm				
PLOT A										
Soybean										
source										
BS	31.8	4.6	5.6	2.1		24.5 a	5.4 a	8.1 a	3.9 a	1.6 a
SM	31.5	6.1	6.2	2.0		31.3ab	5.8 a	9.8 b	4.1 a	1.4 a
TSP	30.3	5.4	6.1	2.5		37.7 b	7.6 b	14.1b	6.5 b	3.5 b
p>F	ns	ns	ns	ns		**	***	*	**	*
rate (kg ha^{-1})										
15	32.6	5.3	6.1	1.9		33.9	6.5	11.5	4.1	2.0
30	30.8	5.7	5.5	2.1		31.1	6.1	9.2	4.0	2.3
60	30.5	5.0	6.3	2.8		28.6	6.3	11.5	4.3	2.2
p>F	ns	ns	ns	ns		ns	ns	ns	ns	ns
0	21.8	2.2	1.5	1.2		22.6	2.1	1.6	0.8	0.9
PLOT B										
Corn										
source										
BS	24.6	3.3	1.5	1.6		25.9 a	5.9 a	5.9	4.7	0.6 a
SM	29.8	3.6	1.9	2.0		31.6ab	7.3ab	6.0	5.0	0.8ab
TSP	29.1	5.6	2.1	2.1		41.2 b	10.2b	8.8	6.0	1.4 b
p>F	ns	ns	ns	ns		*	*	ns	ns	*
rate (kg ha^{-1})										
15	23.3	4.5	1.9	2.0		32.9	7.0	6.0	4.6 a	0.9
30	32.0	3.7	1.8	1.8		31.9	7.6	6.5	5.1ab	1.0
60	29.0	4.2	1.8	2.0		33.9	8.8	8.1	6.1 b	1.0
P>F	ns	ns	ns	ns		ns	ns	ns	ns	ns
0	23.2	2.8	1.5	0.8		24.5	2.8	1.3	1.3	1.0

ns = non significant, * = significant at 0.05 probability level, ** = significant at 0.01 probability level, *** = significant at 0.001 or lower probability level

‡ numbers in columns followed by different letters are significant differently (P>0.05).

Table 4. Soil Phosphorus (Olsen and $CaCl_2$) content in 0 -10, 10-20, 20-30 and 30-40 cm soil depths three weeks after planting corn and soybean (t1) and at harvest (t2) following biosolids (BS), swine manure (SM) and triple superphosphate (TSP) applications at three P rates to a Webster soil in 2002.

	Phosphorus (mg kg^{-1})								
	Olsen								**$CaCl_2$**
	t1				t2				
	0 -10	10 - 20	20 - 30	30 - 40	0 -10	10 - 20	20 - 30	30 - 40	0-10
	cm				cm				
PLOT A ***Soybean*** source									
BS	24.6 **a**	2.8 **a**	1.7	0.8	34.2 **a**	5.3 **a**	1.3 **a**	0.8	3.8
SM	34.2**ab**	4.4**ab**	1.8	0.9	36.7 **a**	6.2 **a**	1.7 **a**	0.8	4.0
TSP	44.2 **b**	6.0 **b**	3.2	0.8	64.3 **b**	12.1 **b**	3.8 **b**	0.9	5.0
p>F	**	*	ns	ns	***	***	***	ns	ns
rate (kg ha^{-1})									
15	38.6	5.4	2.5	0.8	38.3 **a**	7.1	2.2	0.8	3.4 **a**
30	31.6	3.1	1.8	0.8	43.7**ab**	6.7	1.8	0.9	4.1**ab**
60	32.9	3.6	2.5	0.8	53.2 **b**	9.7	2.8	0.9	4.6 **b**
p>F	ns	ns	ns	ns	*	ns	ns	ns	*
0	23.2	2.8	1.5	0.8	24.5	2.8	1.3	0.8	1.1
PLOT B ***Corn*** source									
BS	44.7 **a**	6.4 **a**	1.9 **a**	0.8	41.9 **a**	8.2	4.4	0.8	5.2 **a**
SM	42.8 **a**	7.5 **a**	3.7 **b**	0.8	41.0 **a**	8.1	3.5	0.9	4.9 **a**
TSP	60.8 **b**	11.4**b**	4.2 **b**	0.9	61.3 **b**	12.6	3.7	1.0	8.2 **b**
p>F	***	**	**	ns	***	ns	ns	ns	***
rate (kg ha^{-1})									
15	44.9	8.5	2.7	0.8	45.3 **a**	9.0	2.7	0.9	5.6
30	52.2	8.7	3.5	0.9	48.7 **a**	11.2	3.8	0.8	6.3
60	51.1	8.1	3.5	0.9	54.7 **b**	8.7	5.1	0.9	6.4
p>F	ns	ns	ns	ns	*	ns	ns	ns	ns
0	24.1	2.9	1.5	0.8	27.1	3.2	1.9	0.9	1.2

ns = non significant, * = significant at 0.05 probability level, ** = significant at 0.01 probability level, *** = significant at 0.001 or lower probability level

‡ numbers in columns followed by different letters are significant differently (P>0.05).

CHAPTER 4: UPTAKE OF PHOSPHORUS AND MOLYBDENUM BY CORN (*Zea mays*) AND SOYBEAN (*Glycine max*) DUE TO THE APPLICATION OF BIOSOLIDS, SWINE MANURE, AND TRIPLE SUPERPHOSPHATE IN IOWA

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J. D. Hernandez*, R. Killorn **

Abstract

There is concern over the possible effects of the application of swine manure and biosolids to high phosphorus (P) testing soils. The application of these materials on soils might result in changes in water, soil, and crop quality. Increasing P in the soil may result in a molybdenum (Mo)-P interaction. Molybdenum might be released from sorption sites, enhancing plant uptake. An increase of Mo in ruminant diets may induce a malady called molybdenosis. The purpose of this study was to determine the effect of swine manure (SM) and biosolids (BS) applications on the uptake of P and Mo by plants. A field study was conducted in which BS, SM, and triple super phosphate (TSP) were applied at three rates to a soil with pH > 6.5 and with a high soil P test (STP). Soybean and corn were planted and the following year the crops were rotated. Soil was analyzed for P. Plant materials were analyzed for P and Mo using an inductively coupled plasma mass spectrometer system (ICP-MS) and Cu was determined using atomic absorption spectrophotometry. Differences in plant Mo concentration due to the P source were found in both soybean and corn. Soil P was

* Hernandez, J. D. Research Assistant. Dept. Agronomy, Iowa State University, Ames IA 50011
** Killorn, R. Professor. Dept Agronomy, Iowa State University, Ames IA, 50011

the highest where TSP was applied. In 2001, plant P concentration did not respond to P addition from any source. In 2002, the P source affected soil and plant P and Mo content. In high STP soil, soybean and corn grain Mo uptake was enhanced by the P source, TSP was higher than BS and SM. Application of higher P rates increased Mo concentration in soybean grain. This was not observed in corn grain. Mo concentration in soybean was higher in whole plants than in grain, whereas the opposite was true in corn. The Cu:Mo decreased and was closer to the critical range for molybdenosis in corn grain than in whole plants, suggesting a different effect depending on the part of the corn plant analyzed. In high STP soil, plant Mo uptake was enhanced more by the type of P source applied than by the increase in P rate application.

Introduction

The use of BS and SM as sources of nutrients for crop production is a practice that is currently in use, more as a way of disposing of waste than for their efficient utilization as sources of nutrients. Biosolids and SM managed as a source of nutrients are of importance in areas where sustainable agriculture is practiced. Biosolids and SM have been used as sources of nitrogen (N) and P for years, however, there is conflicting information about the proportions and amounts that can be used by crops and their consequences in the soil-crop system (Frossard et al., 1996).

Summers et al. (1979) conducted a study evaluating the potential of P leaching in soils in Pennsylvania. Minimal P leaching was observed. However, studies have shown that continuous application of BS will result in a build up of heavy metals and P in soil profiles (Peterson et al., 1994; Sui et al., 1999). The same may happen with SM. An increase of soil P above concentrations required for crop production is a concern. An increase of P concentrations in the soil might produce an imbalance in the soil chemical equilibrium and may enhance Mo mobility and subsequently increase plant uptake (Xie and MacKenzey, 1991)

A continuous increase of P in the soil solution might decrease the capacity of the soil to retain phosphorus due mainly to soil P saturation. This can happen due to the P from BS and SM. Under repeated manure application soil has shown the potential for P leaching (Chang et al., 1991; James et al., 1996). Sui and Thompson (2000), in a laboratory investigation, found that the application of BS to high STP soil increased the P concentration in the soil solution, suggesting a decreased ability of the soil to sorb P.

Biosolids and SM applications might increase the movement of P in high P test soils. Phosphorus and Mo are present in the soil primarily in the anionic forms phosphate (HPO_4^- and $H_2PO_4^{2-}$) and molybdate (MoO_4^{2-}) Gupta et al., 1997). These ions have different affinities for sorption sites (Ryden et al., 1987).

The solubility and mobility of Mo in the soil solution are a function of pH, Mo saturation, and competing anions such as phosphate and sulfate (Vleck and Lindsay, 1977). Ryden et al. (1987) and Balistrieri and Chao (1990) in different experiments found that at pH greater than 6.5 in either single-sorbate or multi-

sorbate systems HPO_4^- and $H_2PO_4^{2-}$ anionic sorption out-competed MoO_4^{2-} for oxide surface sites. Most researchers have reported that Mo has low mobility due to its low concentration in the soil solution. However, the mobility of Mo in the soil may be increased by raising pH higher than 6.0, by adding P to high STP soils, and by increasing the soil organic matter content (Jones et al., 1990).

Several studies have shown that the application of BS and manure at appropriate rates in crop production has minimal effects on soil and water quality (Phillips and Grant, 1994). However, repeated manure applications to high STP soils might increase P movement in soil (Chang et al., 1991; James et al., 1996; White and Sharpley, 1996). Consequently, plant Mo uptake is enhanced by the presence of soluble P (Xie and MacKenzie, 1991). Past research has not considered the possible effects of soil P build up on Mo sorption/desorption. A release of Mo from soil sorption sites into the soil solution might cause increased plant uptake. Even though an excess of Mo does not seem to cause toxicity in crops in field conditions (Gupta and Lipsett, 1981), Mo is readily taken up by forage plants and can accumulate to levels detrimental to grazing ruminant animals and produce molybdenosis (Dick, 1956).

Molybdenosis severely affects the digestive system of livestock. Ruminants, particularly cattle, are highly sensitive to this malady (Dick, 1956). It is characterized by an imbalance in animal diets due to the presence of high amounts of Mo and sulfur (S) combined with low concentrations of Cu in animal feed, enhancing Mo induced Cu deficiency (Scott, 1972).

Corn and soybean silage and grain are an important nutritional source for cattle in the US. Swine manure is a by-product commonly applied to farmlands. Thus, the study of the effect of BS and SM on the soil Mo and P relationships are important particularly in the US Midwest. Little in the literature addresses the effects of SM and BS application on high STP soils on Mo availability and plant uptake.

Soybean grain tends to take up larger amounts of Mo compared with corn grain when BS is land applied (McBride et al., 2000). Increasing plant Mo uptake in soybean and corn might make such crops unsuitable for animal consumption due to risk of molybdenosis (Gupta and Lipsett, 1981; Neuman et al., 1987). Molybdenum is present in BS and SM at low concentrations. However, due to the large volumes of BS and SM applied to fields, absolute amounts of Mo applied may be high. The effect of increasing soluble phosphate on plant uptake of Mo in high STP soils needs to be investigated.

The objective of this study was to determine the effects of the application of BS, SM, and triple superphosphate (TSP) to a high STP soil on P and Mo accumulation in soybean and corn whole plants and grain.

Materials and Methods

The experiment was conducted at the Iowa State University (ISU), Department of Agronomy Research farm, where traditional tillage was used in soybean and corn production. The soil was a Webster soil (Fine-loamy, mixed, superactive, mesic Typic Endoaquolls), with organic matter (OM) content of 3.6%, surface pH of 6.5 (Thomas, 1996) and soil test-P (Olsen et al., 1954) of 27 mg kg^{-1}. The soil P level is considered to be high for corn and soybean production in Iowa

(Voss et al., 1996). Biosolids, SM, and TSP (0-45-0) (Table 1) were applied to the field at three rates to supply 15, 30 and 60 kg P ha^{-1}. Swine manure was obtained from the ISU Swine Nutrition Farm and BS from the Water Pollution Control Facility, Ames, Iowa. Ammonium nitrate (NH_4NO_3) was applied in corn plots to equalize the amount of N considering SM and BS initial N credits and a target rate of 120 kg ha^{-1} N. It was assumed that 500 g kg^{-1} of the total N in both BS and SM will be available during crop growing season.

The field was divided into two plots, A and B. The A was a soybean plot and the B a corn plot. Each plot was subdivided into subplots 4 m long x 5 m wide. Swine manure, BS, and TSP were broadcast with manure applicator equipment and incorporated with a cultivator in the spring before the crops were planted. Ten days after the treatments were applied corn (Pioneer 35P12) and soybean (Pioneer 92B62) were planted. Corn was planted at 79,000 plants ha^{-1} and soybean at 380,000 plants ha^{-1}. This experiment was conducted for two soybean-corn cycles in the same area. Soil samples were taken at 0-10 cm depth 15 days after treatment application (t1) and following harvest (t2). The soil analyses included pH (Thomas, 1996) and soil test-P (Olsen et al., 1954).

Whole plant samples were collected from both crops 21 days after planting and when physiological maturity was reached. Five whole plants were cut at ground level. Corn ears were removed before whole plant analysis. Samples were washed, rinsed, acid washed with 0.5 M hydrochloric acid (HCl) and rinsed three times with double de-ionized water (DDIW).

Grain from soybean and corn plots was harvested using two-row combines, one specific for soybean and the other for corn. During harvesting samples of grain were collected. Both whole plant and grain samples were oven dried (60° C for 72 hours), ground with a stainless steel Wiley mill, and sieved through a 40-mesh stainless steel screen. Samples were transferred to a desiccator and stored.

The oven-dried samples were wet digested in concentrated nitric acid (HNO_3) and 50% hydrogen peroxide (H_2O_2) following a method modified from Halvin and Soltanpour (1980). The modification consisted of adjusting the digesting time of plant samples. The digesting process consisted of pre-digesting 0.5 g of ground grain in 5 ml of concentrated HNO_3 in a volumetric flask for 2 hours, and then heating to 220° C for 20 minutes in a closed digesting system. Afterwards, 5 ml of H_2O_2 was slowly added through a capillary funnel. Digestion was continued for 20 additional minutes or the time required to fully digest the sample. The digest was transferred into a 100-ml volumetric flask and brought to volume using DDIW. The diluted digest was filtered through quantitative filter paper and the aqueous extract was analyzed for P, Mo, and Cu.

Phosphorus was determined using the Murphy and Riley method (1962). Molybdenum was determined using an inductively coupled plasma mass spectrometer system (ICP-MS). The ICP-MS system was calibrated to determine the presence of ^{95}Mo isotope, which does not interfere with other isotopes (Jarvis et al., 1992). The samples were spiked and specific certified standards were used for Mo ICP-MS calibration. Sample recovery for standards was within 5% of expected

values. The detection limit for the determination was 2 μg Mo kg^{-1}. Copper was determined using atomic absorption spectrophotometry.

The experiment was conducted for two years, 2001 and 2002. Means for each year were analyzed as a separate experiment. The experimental design was a randomized complete block, with a factorial treatment arrangement of 2 factors, material applied and P rate, and 3 replications. The control treatment, zero application was not statistically compared with the other treatments. The data were analyzed by using analysis of variance (ANOVA). ANOVA was performed using the general linear model (GLM) procedure of the SAS statistical program (SAS Institute, 1999). A probability of 0.05 or less was used to separate significant and non-significant effects. Means of the treatments were compared using Duncan's Multiple Range procedure.

Results and Discussion

Control treatments with no applications are presented for reference, but were not included in the statistical analysis.

Soil Phosphorus

There were no differences in plot A at either t1 or t2 due to treatments in 2001 (soybean following corn). This was expected because similar rates of P were applied. However, at t1 and t2 in 2002 higher accumulations of soil extractable P and significant differences among the treatments were observed. The TSP treatment increased the amount of soil P the most and the BS and SM treatments increased the amount of soil P at t1 and t2 similarly (Table 2). The addition of the higher P rate resulted in a significant increase in soil P (Table 2).

In plot B in 2001 (corn following soybean) the addition of P sources resulted in differences in among the treatments. Triple superphosphate accumulated more P in the soil than SM and BS at t1. However, no differences were observed at harvest time (t2) in the same year (Table 2). The same plot in 2002 showed significant response to treatments. The application of TSP resulted in the highest soil P concentration at both sampling times (Table 2). The application of P at three different rates resulted in significant differences among means at t1 in 2001 and t2 in 2002. Application of the highest P rate resulted in the highest soil P concentration (Table 2).

In 2002, an increase in P rate also increased extractable soil P in plot A and B. In plot A the increase in P rate resulted in higher soil P at both t1 and t2 (Table 2). In plot B, the increase in P rate was only significant at t2 and was only different at the lowest and the highest P rates (Table 2).

Past research has indicated that repeated SM and BS applications to high STP soils increased extractable soil P in comparison with inorganic sources. This appears to be primarily due to soil P saturation and ion competition of inorganic and inorganic products found in SM and BS with P sorption sites (Chang et al., 1991; James et al., 1996; White and Sharpley, 1996; Gupta, 1997, Sui and Thompson, 2000). Under the experimental conditions, we did not observe this result. Instead extractable soil P was higher in TSP treatments than the other treatments.

Corn and Soybean Grain

Phosphorus in Grain

The amount of P in corn and soybean grain did not increase significantly in 2001 regardless of the source. An average concentration of 5185 mg kg^{-1} in soybean and 1617 mg kg^{-1} in corn seemed to be sufficient for crop development (Jones et al., 1991) in 2001 (Table 3). Phosphorus concentration in corn and soybean grain was generally lower in 2002 compared to 2001. This response might be attributed to environmental conditions; 2002 was drier than 2001. Water plays an important role in the P uptake by plants.

The average grain P concentration in 2002 was 4215 mg kg^{-1} in soybean and 1110 mg kg^{-1} in corn (Table 3). There was a tendency for P to increase in the soybean grain in parallel to the soil P concentration (Table 2). However, yield response differences were not observed in either year at any level of the treatments.

Molybdenum in the grain

Molybdenum concentration in soybean grain was not affected by the source of P applied in 2001. The Mo concentration in soybean in 2001 averaged 2.61 mg kg^{-1}. Lavado et al. (2001) found grain Mo concentration in soybean under traditional tillage to be in the range of 1.7 to 2.9 mg kg^{-1} in an Argentine Mollisol. In 2002 the Mo concentration in soybean grain increased in all the treatments almost 100% compared to 2001 (Table 3). This increase implies that a rotation effect of soybean following corn is present. Previous research also recognized the effect of rotation on plant Mo accumulation (Gupta 1997; O'Connor and McDowell, 1999; O'Connor, et al., 2001a).

In 2002, Mo concentrations in soybean grain were higher in SM and TSP treatments than BS treatments (Table 3). This result was not expected, because the Mo content in BS was higher than TSP (traces) and SM (Table 1). The Mo concentration of soybean grain in 2002 was greater than 5.0 mg kg^{-1} in all treatments that received BS, SM, and TSP. The average Mo concentration of soybean grain in the control plots was 3.81 mg kg^{-1}. Dick (1956) considered this value as critical for molybdenosis. In our experiment the tendency for Mo to increase in response to the treatments was observed.

Molybdenum concentration in corn grain was less than soybean grain in both years (Table 3). Other researchers have found similar results (O'Connor et al., 2001a; McBride et al., 2000; Jones et al., 1991; Vleck and Lindsay, 1977). Molybdenum concentration decreased slightly in 2002 in corn plants in BS and SM application. No differences in plant Mo were observed in TSP treatments.

The increase of P rate did not cause significant differences in P and Mo concentration in corn grain content in either year (Table 3). This result suggests that corn Mo uptake was not affected by an increase in P rate.

Copper and Copper/Molybdenum ratio

Traditionally, Mo concentration in plant and grain has been related to molybdenosis. However, Mo concentration alone is not an effective parameter to estimate potential risk of molybdenosis. Rather than the Mo concentration in plant and grain, it is the relationship between Cu and Mo in the cattle diet that defines this problem (Ward, 1994; O'Connor et al., 2001ab). A low Cu:Mo (close to 2:1) indicates a higher risk of molybdenosis (Ward, 1994).

The Cu concentration in soybean grain harvested in this project in 2001 was about 15 mg kg^{-1} and 14 mg kg^{-1} for 2002 and was not affected by any BS, SM, or TSP treatment (Table 3). This value is considered sufficient for soybean development (Jones et al., 1991). O'Connor et al. (2001a) found similar Cu concentrations in soybean grain harvested from soils treated with BS.

The Cu:Mo in soybean grain was not affected by source in 2001 (Table 3). In 2002, the ratio decreased, due mainly to an increase in Mo concentration in grain. Additionally SM and TSP treatments had the lowest ratio whereas BS was the highest (Table 3). This result was not expected. We were expecting BS to decrease the Cu:Mo, because it had higher Mo concentration than the other sources.

The Cu concentration in corn grain averaged 1.9 mg kg^{-1} in 2001 and 0.9 mg kg^{-1} in 2002 (Table 3) and was not affected by treatments either year. Previous research reported Cu concentration ranges between 7 to 10 mg kg^{-1} (Lavado et al., 2001) in corn grain. Copper concentration in grain tends to be low when it is present in low quantities in the soil (Nambiar, 1976).

The low Cu concentration in corn grain in 2001 and the even lower concentration in 2002 cannot be explained in this paper. However, it may be related to the corn hybrid used, a depletion of soil Cu, or some environmental cause. Regardless of the reason, this reduction in the Cu concentration in the corn grain contributed to a reduction in the Cu:Mo ratio in the corn grain. The Cu:Mo was lower in the TSP treatments than in the BS and SM treatments (Table 3). We were expecting a lower ratio in BS and SM treatment means due to the higher Mo concentration in those sources.

Increasing the rate of P application in corn plots did not affect Cu concentrations in the grain of either crop in either year (Table 3). On the other hand, Cu:Mo decreased at the highest P rates. This suggests that at a higher P application rate more Mo was available to the plant. There was a reduction of Cu:Mo in corn and soybean grain in 2002. This Cu:Mo ratio reduction in soybean and corn grain

indicates a potential risk for molybdenosis. However, the risk is applicable if only grain is used in cattle diets.

Corn and Soybean Whole Plant

Phosphorus and molybdenum

The P concentration in soybean whole plants increased the most in TSP treatments in 2001 and 2002 (Table 4). This suggests greater plant P uptake from TSP than from SM and BS. The soybean whole-plant P concentration in TSP treatments is considered to be in the high range (Jones et al. 1991), suggesting luxury consumption of P by the plant. This may be explained by the higher extractable soil P found in TSP treatments (Table 2). Molybdenum concentration in soybean and corn whole plants was not affected by source applied in 2001. However, in 2002 the Mo concentration in soybean was the highest in TSP treatment (Table 4). This suggests that in high STP soil conditions the use of TSP may enhance Mo plant uptake by soybean plants.

The Mo concentration in corn whole-plants was relatively higher in all the treatments in 2002 compared with 2001. The increase in Mo concentration was about 50 % in BS, 35 % in SM and 75 % in TSP treatments. This result was not consistent with O'Connor et al. (2001b). They found no Mo accumulation in corn stover after continued BS application and very low Mo concentration.

There were no differences in corn whole-plant P concentration due to the treatments in 2001 or 2002. Phosphorus concentration in corn plants was slightly higher in TSP treatments, however the difference was not significant (Table 4). In 2002, Mo concentration in whole-plants soybean increased more with the TSP and

BS applications than with the SM applications (Table 4). This suggests that high STP and the addition of either TSP or BS may enhance Mo plant uptake. We were expecting this result with BS. However, Mo increase in whole-plants after TSP was applied cannot be explained. Increasing the rate of P application did not affect Mo plant concentration in corn and soybean plants in either year (Table 4).

Copper and copper:molybdenum ratio

Copper concentration in soybean and corn plants was not affected by the addition of TSP, SM and BS. However, in 2002 Cu concentration in soybean whole plants was relatively lower than in 2001 (Table 4). The plant Cu concentrations in corn and soybean plants were within the normal growth range (Jones et al 1991). In 2002, the source of P had an effect on the corn and soybean Cu:Mo. Triple superphosphate and BS application changed the Cu:Mo in soybean in 2002. This result suggests that BS and TSP would increase molybdenosis risk more than did SM.

In whole corn plants Cu:Mo was relatively lower in 2002 than in 2001. There were no differences among Cu:Mo means related to the application of TSP, SM and BS in 2001. Super triplephosphate application changed Cu:Mo the most in 2002 (Table 4). Finally, the rate of P application did not affect either Cu or Cu:Mo in corn and soybean whole plants in either year (Table 4).

Summary and Conclusions

The soil P concentration measured by the Olsen extraction was not increased after BS, SM, and TSP were applied in 2001. However, in 2002 the addition of P sources resulted in soil P accumulation in all treatments. Triple superphosphate increased extractable soil P more than BS and SM treatments.

Phosphorus concentration in corn and soybean grain was not affected by the treatments in 2001. In 2002, applications of SM and TSP increased corn grain P uptake more than did applications of BS. Molybdenum in soybean grain increased in 2002 with SM and TSP treatments. Triple superphosphate and SM were the treatments that produced the highest Mo concentrations in corn and soybean grain. A higher Mo grain uptake in soybean was observed in the second year of the rotation. Higher application of P rates did not increase P and Mo in corn grain in either year.

Increasing P application rate increased P and Mo concentration in soybean grain in 2002. An increase of Mo concentration after using TSP at the highest P rate suggests that increasing P in high STP soil may increase Mo plant uptake in soybean grain.

The Cu:Mo ratio in corn and soybean grain was affected by the addition of P sources only in 2002. Biosolids application caused a decrease in Cu:Mo, suggesting that BS is the source with the highest risk of inducing molybdenosis of all of the three sources. The Cu:Mo decrease in soybean grain from 2001 to 2002 was attributed to an increase in grain Mo uptake, while in corn grain it was due to a decrease in Cu concentration.

There were no differences in Cu:Mo in corn grain treatments as a result of the treatments in 2001. In 2002, Cu:Mo in corn grain was reduced most with the TSP treatments.

When Cu:Mo ratio is considered to assess molybdenosis risk, corn grain presented a higher risk than soybean for use in bovine diets. However, the corn grain Mo concentration remained relatively low, while soybean grain Mo concentration was relatively high.

The type of P source applied enhanced Mo grain concentrations in soybean and corn; Triple superphosphate was higher than BS and SM. Phosphorus rate application increased Mo uptake in soybean grain. This was not observed in corn grain.

Phosphorus concentrations in corn and soybean plants were higher with TSP than with SM and BS application. Molybdenum concentration in plants increased with the BS and TSP application more than SM. Source had a greater effect on Mo uptake in plants than did P rate.

Neither P source nor the rate of P application on the treatments affected copper concentration in plants. Whole corn plants had higher Cu concentration than did grain. The Cu:Mo relationship was decreased more with TSP and BS than SM. A risk assessment of molybdenosis might be different when considering grain or whole plant. In high STP soils plant and grain Mo concentrations were increased more by the type of P source applied than by increasing P rate.

Application of BS, SM, and TSP to a high STP soil resulted in an increase of soil P, however, this increase of soil P did not result in an increase of either grain or whole plant Mo uptake in corn. The increase of plant Mo uptake in corn was due mainly to the application of BS and SM. Increasing P application rate increased P and Mo concentration in soybean whole plant and grain. An increase of Mo concentration after using TSP, and at the highest P rate, suggests that increasing P in high STP soil may increase molybdenum plant uptake in soybean grain.

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Table 1. Selected chemical characteristics of biosolids and swine manure used in this study.

	Biosolids		Swine manure	
	Year			
	2001	2002	2001	2002
Total solids (g kg^{-1})	24.8	23.6	11.1	12.1
Total N (g kg^{-1}) *	2.0	2.6	2.5	3.6
Total P (g kg^{-1}) *	0.6	1.2	0.5	0.8
Total Ca (g kg^{-1}) *	120	230	27	84
Total Fe (mg kg^{-1}) *	530	856	35	73
Total Al (mg kg^{-1}) *	172	285	24	390
Total Mo (mg kg^{-1}) *	13.1	14.1	0.7	0.8

* wet basis

Table 2. Phosphorus (Olsen) content in an Iowa soil after biosolids (BS), swine manure (SM) and triple superphosphate (TSP) were applied at three equivalent P rates, soil samples collected three weeks after planting (t1) and harvest (t2) in plots A (soybean following corn), and B (corn following soybean).

	Year			
	2001		2002	
	time			
	t1	t2	t1	t2
	P (Olsen)			
PLOT A				
	mg kg^{-1}			
	Soybean		Corn	
source				
BS	32.6	29.5	44.7 **a**	41.9 **a**
SM	30.8	31.0	42.8 **a**	45.0 **a**
TSP	30.5	33.9	60.8 **b**	61.3 **b**
p>F	**ns**	**ns**	***	*
rate (kg P ha^{-1})				
15	32.6	29.5	25.1 **a**	31.4 **a**
30	30.8	31.0	29.7 **b**	32.1 **a**
60	30.5	33.9	30.1 **b**	33.9 **b**
p>F	**ns**	**ns**	*	*
0	23.8	24.6	25.2	19.0
PLOT B				
	Corn		Soybean	
source				
BS	17.9 **a**	28.0	24.6 **a**	34.2 **a**
SM	31.4 **b**	27.0	34.2**ab**	36.7 **a**
TSP	37.8 **c**	29.0	44.2 **b**	64.2 **b**
p>F	*	**ns**	**	***
rate (kg P ha^{-1})				
15	17.9 **a**	28.0	38.5	38.3 **a**
30	31.4 **b**	27.0	31.6	43.7**ab**
60	37.8 **c**	29.0	32.6	53.2 **b**
p>F	*	**ns**	**ns**	*
0	22.9	24.5	20.8	21.0

ns = non significant, * = significant at 0.05 probability level, ** = significant at 0.01probability level, *** = significant at 0.001 or lower probability level

‡ numbers in columns followed by different letters are significantly different (P>0.05).

Table 3. Phosphorus, molybdenum, and copper content of corn and soybean grain afterbiosolids, swine manure and triple superphosphate were applied at three equivalent P rates to a soil in Iowa.

	2001				2002			
	P	*Mo*	*Cu*	*Cu:Mo*	*P*	*Mo*	*Cu*	*Cu:Mo*
		mg kg^{-1}				mg kg^{-1}		
Soybean								
source								
BS	5094	2.5	15.1	6.1	4124 a	5.0 a	14.0	2.8 b
SM	5228	2.8	15.3	5.8	4224 b	5.7 b	13.8	2.4 a
TSP	5233	2.5	15.6	6.4	4296 b	5.6 b	13.6	2.4 a
p>F	ns	ns	ns	ns	*	*	ns	**
rate (kg P ha^{-1})								
15	5124	2.5	15.1	6.1	4091 a	5.1 a	13.6	2.7 b
30	5181	2.7	15.1	6.0	4342 b	5.6 b	13.8	2.4 a
60	5250	2.7	15.8	6.2	4208 b	5.7 b	13.6	2.3 a
p>F	ns	ns	ns	ns	*	***	ns	**
0	4420	2.5	15.1	6.1	3850	5.0	13.8	2.8
Corn								
source								
BS	1547	1.0 b	1.9	1.9	1032 a	0.8 a	0.8	1.0 b
SM	1511	1.0 b	2.3	2.2	1042 a	0.8 a	1.2	1.3 b
TSP	1793	0.9 a	1.3	1.4	1257 b	0.9 b	0.7	0.7 a
p>F	ns	*	ns	ns	*	*	ns	*
rate kg P ha^{-1}								
15	1488	1.0	1.8	1.8	1058	0.8	0.7	0.9
30	1890	1.0	2.1	2.0	1118	0.8	0.8	0.9
60	1472	1.0	1.8	1.6	1155	0.9	1.1	1.2
p>F	ns	ns	ns	ns	ns	ns	ns	ns
0	1520	1.0	1.8	1.9	996	0.8	0.7	0.9

ns = non significant, * = significant at 0.05 probability level, ** = significant at 0.01probability level, *** = significant at 0.001 or lower probability level

‡ numbers in columns followed by different letters are significantly different (P>0.05).

Table 4. Phosphorus, molybdenum, and copper content of corn and soybean whole plant after biosolids, swine manure and triple superphosphate were applied at three equivalent P rates to a soil in Iowa.

	2001				2002			
	P	Mo	Cu	Cu:Mo	P	Mo	Cu	Cu:Mo
		mg kg^{-1}				mg kg^{-1}		
Soybean								
source								
BS	4603 a	2.5	13.9	5.6	4418 a	2.4 b	9.4	4.0 a
SM	4785 a	2.2	13.6	6.2	4382 a	1.9 a	9.4	5.0 b
TSP	5554 b	2.2	13.8	6.4	4598 b	2.7 c	9.1	3.4 a
p>F	*	ns	ns	ns	*	***	ns	*
rate (kg P ha-1)								
15	4727 a	2.3	14.2	6.3	4436	2.3	9.2	4.0
30	4931ab	2.4	13.9	6.1	4418	2.2	9.4	4.3
60	5241 b	2.3	13.2	5.9	4544	2.3	9.3	4.2
p>F	*	ns	ns	ns	ns	ns	ns	ns
Corn								
source								
BS	2596	0.7	6.1	9.1	3060	1.1 b	6.7	6.1 b
SM	2588	0.7	5.6	8.5	2902	1.0 a	6.3	6.6 b
TSP	2624	0.7	5.8	9.1	3142	1.1 b	6.4	5.6 a
p>F	ns	ns	ns	ns	ns	*	ns	*
rate (kg P ha^{-1})								
15	2629	0.8	5.9	7.8	3033	1.0	6.7	6.7
30	2566	0.6	5.9	9.8	2996	1.0	6.2	6.4
60	2609	0.7	5.8	9.0	3076	1.1	6.5	5.9
p>F	ns	ns	ns	ns	ns	ns	ns	ns

ns = non significant, * = significant at 0.05 probability level, ** = significant at 0.01probability level, *** = significant at 0.001 or lower probability level

‡ numbers in columns followed by different letters are significantly different (P>0.05).

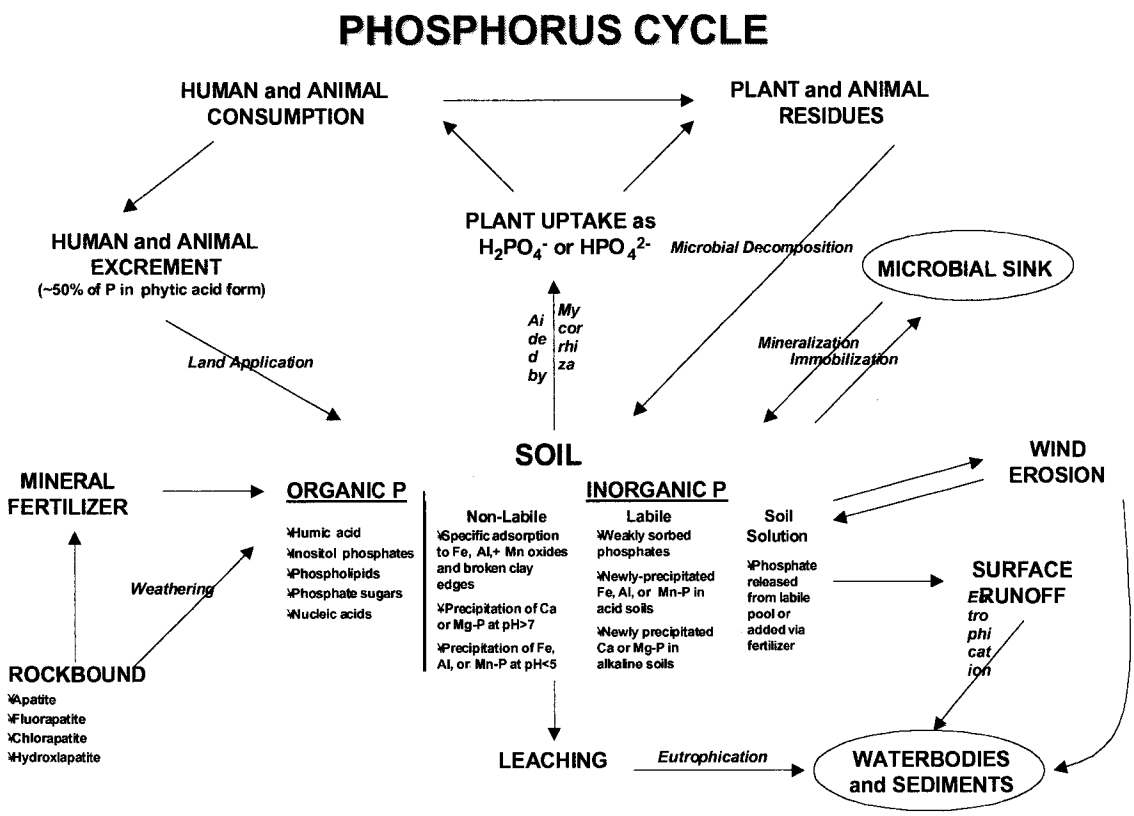
CHAPTER 5. GENERAL CONCLUSIONS

Land application of BS, SM, and TSP is a common practice, even in high STP soils. This investigation included a soil incubation study, a study field, and plant response in the field study. The application of BS, SM, and TSP to a high STP soil resulted in an increase of soil P. This increase of soil P did not result in increases in extractable Mo. The effect of the application of BS, SM, and TSP to high-soil test P soils was to increase P build up, but this increase did not effect soybean and corn plant Mo accumulation.

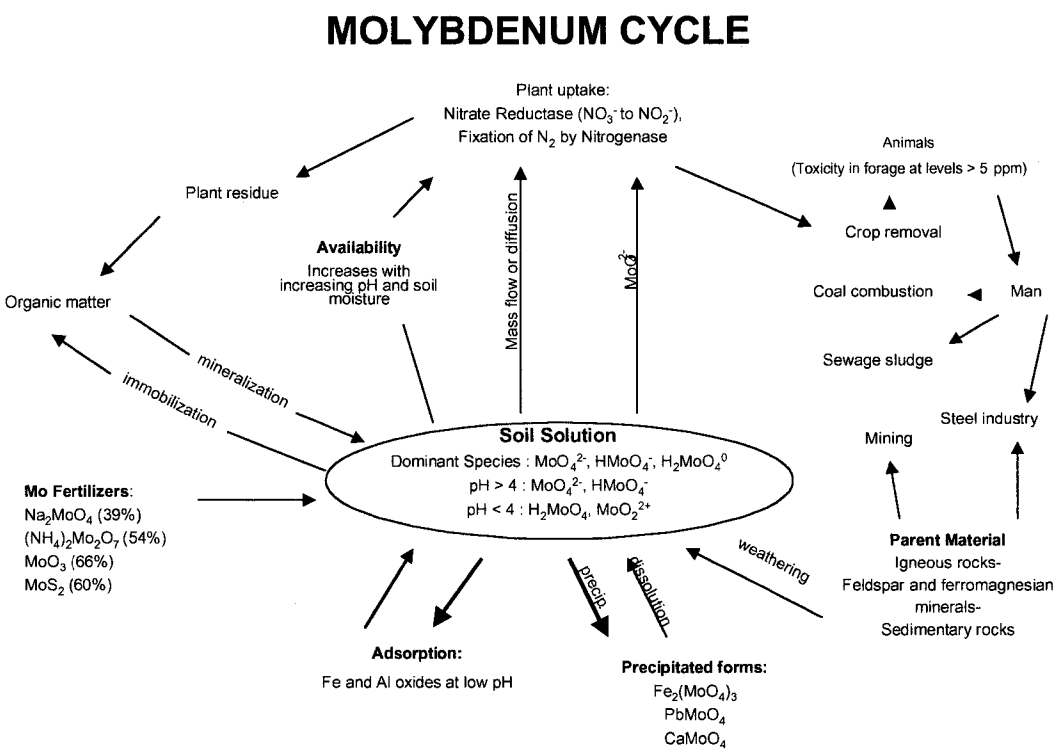
Treatments did not cause an increase of either grain or Mo uptake in corn. However, increasing P application rate increased P and Mo concentration in soybean whole plant and grain. An increase of Mo concentration after using TSP, and at the highest P rate, suggests that increasing P in high STP soils may increase Mo plant uptake in soybean grain.

The results of this study suggest that the fate of P and Mo after 2 years of application of BS and SM is an accumulation in the soil plant system. Accumulations of P in already high STP soils may lead to potential movement of P off-site. This P movement out of sorption sites may contribute to the already high P surplus in the ecosystem. Accumulations of Mo in the soil and subsequently in soybean may increase the potential for molybdenosis in livestock that use soybean as main source of protein.

APPENDIX A. PHOSPHORUS CYCLE



APPENDIX B. MOLYBDENUM CYCLE



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BIOGRAPHICAL SKETCH

Jorge David Hernandez was born July 21, 1966 in Caracas DF, Venezuela. He received a technical degree in Agriculture (Plant production) from Gervasio Rubio Institute in State of Tachira, Venezuela in 1984, and his Bachelor in Agronomy ("Agronomy Engineer" with a major in Phytotecny; thesis in Soil science) from Central University of Venezuela in 1992. He was awarded the PIGMALION in 1996 (World Bank and FONAIAP). He has served in INTEVEP-Internship program from 1991 to 1992 (Venezuelan Oil Corporation Research Center), PALMAVEN (Venezuelan Petroleum Corporation known in the United States as CITGO Co.) as Technical Assistant from 1992 to 1993, Del Monte Food-Venezuela (Philip Morris Co.) as Agricultural Supervisor in 1992, FONAIAP (National Agricultural Research Center of Venezuela) as a Researcher from 1994 to1996, and at Iowa State University in the department of Agronomy as a Research Assistant from 1996 to 2003.